orange solid, mp 314–316°, also shown to be the cis diiodide.[46] These two polymorphs were separated by fractional recrystallization from chloroform. No Pt–Cl stretching band was observed in the infrared spectrum of the yellow powder; the rest of the spectrum was nearly identical with that of *cis*-$Pt(Ph_3P)_2Cl$.

Preparation of *trans*-$Pt(Ph_3P)_2X_2$. The trans isomer of $Pt(Ph_3P)_2Cl_2$ was prepared from the cis isomer by photochemical methods.[13] Lemon-yellow crystals, mp 306–309° (lit.,[47] 307–310°), were produced by recrystallization from benzene. A single strong Pt–Cl stretching band at 344 cm^{-1} was observed in the infrared.[46]

The trans dibromide was prepared by metathesis of the trans dichloride with excess LiBr (1:100, mol) in refluxing ethanol–water (100:1, v/v) with periodic addition of small portions of chloroform, to give a dark yellow solid, mp 309–310°, with no Pt–Cl band in the infrared. The remaining infrared spectrum was nearly identical with that of the trans dichloride.

Metathesis of the trans dichloride with excess NaI (1:500, mol) in a refluxing mixture of water, acetone, ethanol, and chloroform (2.5:1:1:1, v/v) gave a yellow-orange powder, mp 296–299°, on evaporation of the chloroform layer; no Pt–Cl band was found in the infrared.

Acknowledgments. We wish to thank Dr. P. A. Turley for providing samples of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ and $Pt(bipy)Cl_2$, Dr. K. Stark for the sample of $Pt(dpm)Cl_2$, Mrs. Sharon M. Jones and Dr. M. Haugh for assistance in obtaining the mass spectra, and Drs. D. A. Lightner and R. A. Kent for many helpful discussions.

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An Oxygen-17 Nuclear Magnetic Resonance Study of Nickel(II)–Ethylenediaminetetraacetate Complexes in Aqueous Solution

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Abstract: At pH 2 the nickel(II)–EDTA complex appears to exist as $Ni(H_2O)HEDTA^-$ with one (protonated) acetate arm replaced by a water molecule. Kinetic parameters for water exchange with this species are $k_1(25°) = (2.0 \pm 0.1) \times 10^5\ sec^{-1}$, $\Delta H^{\ddagger} = 9.8 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -1.5 \pm 2$ cal mol^{-1} deg^{-1}. The scalar coupling constant A/h for the Ni–O interaction is $(2.3 \pm 0.1) \times 10^7$ Hz. At pH 6–7, evidence for significant amounts of an aquo–EDTA complex was found. It was concluded that a six-coordinate species, $Ni(H_2O)(EDTA)^{2-}$, with one unprotonated acetate arm off, best explains the observations. Kinetic parameters for this species are $k_1(25°) = (7 \pm 0.5) \times 10^5\ sec^{-1}$, $\Delta H^{\ddagger} = 8.0 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -7.0 \pm 2$ cal mol^{-1} deg^{-1}. The scalar coupling constant A/h is $(2.6 \pm 0.2) \times 10^7$ Hz. Effects of substitution on water lability are discussed as well as structural implications. The nickel(II)–ethylenediaminedisuccinic acid (EDDS) complex also appears to have a small percentage of aquo form present at high pH.

The crystallographic studies on transition metal–EDTA (ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate, H_4Y) complexes by Hoard and his group[1] showed structural possibilities A–D in the solid state (Figure 1). Except in the case of substitution-inert cobalt(III) compounds,[2] the structure of these complexes in solution is still an unsettled question.

The common p*K* value exhibited toward protonation led Higginson[3] to postulate that the divalent metal complexes had structure B both in the protonated and unprotonated forms. Colorimetric studies of Nancollas[4] shed doubt on this conclusion. Bhat and Krishnamurthy[5] deduced from the pH dependence of the electronic spectra of Ni(II), Co(II), and Cu(II) complexes that at neutral pH at least some of the EDTA was hexadentate (structure A) and that one carboxylate arm was removed by protonation. The predominant outer-sphere oxidation[6] of Co(II)–EDTA solution to the inert Co(III)–EDTA ion (Fig. 1A) suggests that in neutral solution Co(II)–EDTA has structure A also. Margerum and Rosen[7] have observed temperature-jump relaxation of Ni(II)–EDTA solutions at pH 8 and conclude that there is a coordinated water molecule present. Matwiyoff,[8] from a combination of ^{13}C and ^{17}O nmr data, concluded that the nickel–EDTA complex has structure A in neutral solution and B in acid solution. Higginson and Samuel,[9] on the other hand, deduce from the formation constants of monodentate ligands with EDTA complexes in neutral solution that for several divalent metals an equilibrium exists between hexadentate (structure A) and pentadentate (structure B) forms.

We have used ^{17}O nmr to investigate the structures and water-exchange kinetics of Ni(II)–EDTA solutions.

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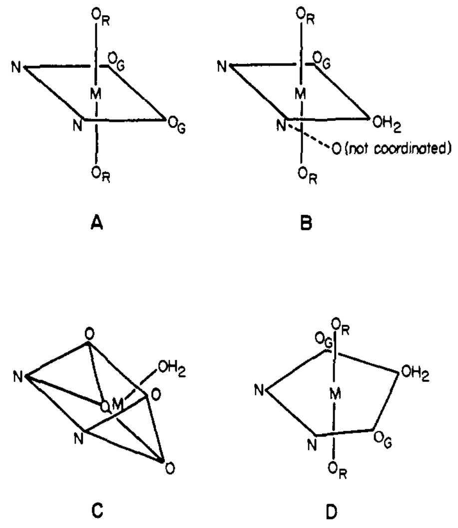

Figure 1. Idealized structures of EDTA complexes in the compounds (A) $NH_4CoY \cdot 2H_2O$, (B) $NiH_2Y \cdot H_2O$, (C) $Mn_3(HY)_2 \cdot 10H_2O$, and (D) $Li[FeY(H_2O)] \cdot 2H_2O$.

Experimental Section

Nickel solutions were prepared from Mallinckrodt AR $Ni(NO_3)_2 \cdot 6H_2O$ and the purity was checked by EDTA titration. EDTA was used without further purification as the Baker Analyzed disodium salt. Solutions for nmr measurements were made up from stock solutions prepared by treating a 1:1 metal ion–EDTA solution with NaOH to give the required pH, adding buffer if necessary, and making up to a standard volume. The water was removed rrom the stock solution *in vacuo* and replaced with ^{17}O-labeled water.

The water was obtained from YEDA R and D Co., Ltd., Rehovot, Israel, and contained *ca.* 7 atom % ^{17}O (normal H content), except for a few shift measurements, where a blank containing 18% ^{17}O was used. The water was doubly distilled *in vacuo* before use.

The buffer was 0.1 *M* potassium hydrogen phthalate at pH 4 and 0.1 *M* phosphate mixtures at pH 6 and 7. Blank solutions contained 0.1 *M* buffer at pH 6 and 7 and 10^{-2} HCl at pH 2.

The nmr equipment has been described.[10] Except where otherwise stated, all measurements were made at 11.5 MHz. The solutions were thermostated by means of a silicone oil circulating system. Temperatures were measured with a Digitemp digital thermometer placed inside the probe, and are believed accurate to ±0.3°.

Results

A preliminary report of these results has appeared.[11]

(a) Acid Solution. The paramagnetic shifts and line broadening data for a nickel–EDTA solution of pH 2.2 are shown in Figures 2 and 3. At this pH, a pH titration shows about one proton per EDTA molecule. Shifts are plotted as the function $Q = TS(M_{H_2O})/(M_{Ni})$, 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. Line broadening data are plotted as $T_{2p}' = 2(M_{Ni})/\gamma\Delta$, where γ is the magnetogyric ratio of ^{17}O (3628 G^{-1} sec^{-1}) and Δ is the line broadening, $W - W_0$; W is the full line width at half-maximum for the nickel solution and W_0 is the same for the blank.

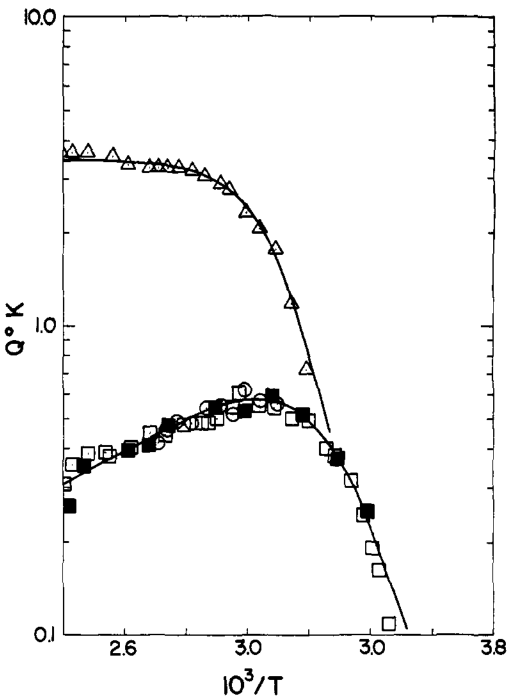

Figure 2. Semilogarithmic plot of the shift function Q against $1/T$ for nickel(II)–EDTA solutions. The continuous curves are the computed fits: (△) pH 2.1, $M_{Ni} = 0.242$; (□) pH 6.1, $M_{Ni} = 0.584$; (○) pH 6.1, $M_{Ni} = 0.462$; (■) pH 7.2, $M_{Ni} = 0.625$.

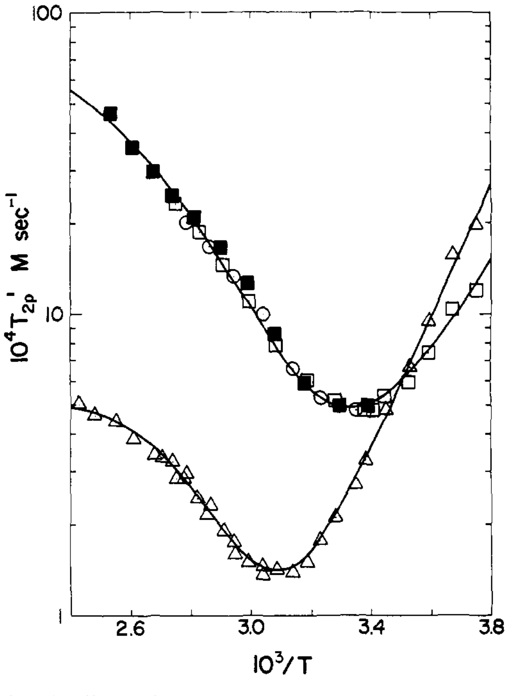

Figure 3. Semilogarithmic plot of T_{2p}' against $1/T$ for nickel(II)–EDTA solutions. The continuous curves are the computed fits: (△) pH 2.1, $M_{Ni} = 0.242$; (□) pH 6.1, $M_{Ni} = 0.584$; (○) pH 6.1, $M_{Ni} = 0.462$; (■) pH 7.2, $M_{Ni} = 0.625$.

The data show behavior typical of a single octahedral nickel species, and shift and line broadening are well accounted for by the full Swift–Connick equation[12] with contributions to the relaxation from both the "$\Delta\omega$" and "T_{2M}" mechanisms. The continuous curves in Figures 2 and 3 represent computed fits to the data. Assuming one water molecule per nickel atom, data treatment in the normal way yields the parameters shown in Table I. The scalar coupling constant is typical of a nickel–water molecule bond in an octa-

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Table I. Parameters Derived from ^{17}O Nmr Data

Species	$k(25°)$,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	A/h, Hz	$T_{1e}(25°)$, sec	E_a for T_{1e}, kcal mol^{-1}
$M(H_2O)YH^-$	$(2 \pm 0.1) \times 10^5$	9.8 ± 0.3	(-1.5 ± 2)	$(2.3 \pm 0.1) \times 10^7$	$(2.8 \pm 0.5) \times 10^{-12}$	0.5 ± 0.5
$M(H_2O)Y^{2-}$	$(7 \pm 0.7) \times 10^5$	8.0 ± 1.0	(-7.0 ± 3)	$(2.6 \pm 0.2) \times 10^7$	$(3.5 \pm 0.5) \times 10^{-12}$	0.0 ± 0.5

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

hedral environment. In acid solution, therefore, we confirm earlier proposals[5,8] that the complex has structure B, the free carboxylate arm being protonated.

(b) Neutral Solution. Shifts and line broadening data are shown in Figures 2 and 3. The results are the same for pH 6.2 and 7.2 using nickel 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 marked difference from the "normal" low-pH results is apparent. Both Q and T_{2p} are smaller, and Q does not increase to a limiting value with increasing temperature but goes through a maximum. A self-consistent and convincing model accounting for the results was obtained using the equilibrium postulated by Higginson and Samuel[9] at high pH, *viz.*, $MY^{2-} + H_2O \rightleftharpoons MY(H_2O)^{2-}$, in which MY^{2-} has structure A and $MY(H_2O)^{2-}$ has structure B. At 25° they find *ca.* 25% of the nickel in the latter form. This form then accounts for the observed shifts and line broadenings. The value of A/h calculated from our data depends on the percentage of structure B assumed and its temperature dependence. If we assume that A/h is $2.4 \pm 0.2 \times 10^7$ Hz for nickel–water interactions in "octahedral" coordination,[13] we can fit our data using 25 ± 3% of form B at 25° and ΔH for the above equilibrium equal to -2.9 kcal mol^{-1}. We cannot specify very precisely the equilibrium amounts (*ca.* ±10%), but our results are basically also in good agreement with the ideas of Higginson and Samuel.[9] One would expect A/h values to be much smaller for outer-sphere interactions and significantly different for nonoctahedral geometries.[14] Assuming one coordinated water molecule per nickel atom in the aquo species, the parameters obtained from curve fitting are given in Table I.

Discussion

Earlier studies[4,7] on these systems will need reconsideration in the light of the newer results. The kinetic data of Margerum and Rosen[7] on ammonia addition are in this category. Their rate constant k_{12}, corrected for the true stoichiometry, is *ca.* 2×10^3 M^{-1} sec^{-1}. In the treatment used by Margerum, the outer-sphere constant (K_{os}) would be *ca.* 3×10^{-3}, which is much smaller than the normal value of 0.017. Possibly the temperature-jump data actually refer to a ring-closing process rather than to substitution.

The apparent inconsistency with the results of Matwiyoff, *et al.*, is believed to be caused by a medium effect.[15] Their studies were made at high salt concentrations where water activity is lowered.

Howard and Marianelli[16] have obtained somewhat similar shift curves in the cobalt(II) chloride–pyridine system and similarly interpret their data in terms of a shifting equilibrium.

We have also examined the ^{17}O nmr of a 0.6 *M* solution of nickel(II)–EDDS (ethylenediamine-*N,N'*-disuccinic acid)[17] at a pH of 6.2. This ligand is isomeric with EDTA but forms a hexadentate complex in which two of the chelate rings are six-membered. There is considerable evidence from molecular models and crystal parameters that the five-membered G rings (Figure 1A) in the EDTA complex are strained, and it was anticipated that EDDS might be less strained and more readily adopt a hexadentate structure in solution. In fact, a small line broadening was observed but no paramagnetic shift; the line broadening was only about one-sixth of that found for an equimolar neutral solution of the EDTA complex and had a similar temperature dependence. It is tempting to suggest that nickel(II)–EDDS predominantly adopts structure A in solution, as expected, with perhaps a few per cent of a hydrated form to account for the small degree of line broadening.

Since this paper was completed, a new study of Ni(II)–EDTA has appeared.[18] The latter group apparently was not aware of ref 9. They state that the proton nmr "spectra can be rationalized as consistent with coordination numbers anywhere between 5 and 6." Our conclusions are considerably firmer than this.

A detailed discussion of effects of substitution on water lability as determined by ^{17}O nmr kinetic studies has been given elsewhere.[19] The $k_1(25°)$ value for $Ni(H_2O)HEDTA^-$ of 2×10^5 sec^{-1} compares with a k_1 (per water) for $Ni(H_2O)_6^{2+}$ at pH 3 of 3.4×10^4 and with k_1 for $Ni(H_2O)_4en^{2+}$ of 4.4×10^5. The labilizations observed might be attributed solely to the nitrogen donors present. Studies on the cobalt–malonate system[20] show that a carboxylate group increases $k_1(25°)$ by about one-half as much as an ammine nitrogen. The $\Delta H^{\ddagger}$ values for the three nickel complexes above are 9.8, 12.0, and 10.0 kcal mol^{-1}, respectively, again suggesting that the acetate arms have small effects for nickel. Such a conclusion must not be taken too seriously, however, as considerable structural differences in highly chelated and less chelated species

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must exist. Also, on deprotonation to give $Ni(H_2O)(EDTA)^{2-}$, the $k_1(25°)$ goes up to 7×10^5 and $\Delta H^{\ddagger}$ goes down to 8.0, which facts suggest that the acetate arms do interact significantly with nickel and/or that solvation and entropy effects are also important. At 25° the labilizing effects of ligands correlate roughly with their electron-donating or -accepting properties but, as discussed in ref 19, the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are difficult to rationalize on this basis alone.

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Reaction of Ethylenediamine and *C,C,C′,C′*-Tetramethylethylenediamine with Glyoxylate in the Presence and Absence of Zinc(II) or Nickel(II)[1]

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Abstract: Glyoxylate reacts with ethylenediamine dihydrochloride (en·2HCl) and *C,C,C′,C′*-tetramethylethylenediamine dihydrochloride (temeen·2HCl) to form 1:1 adducts which are considerably more stable and acidic than Schiff bases. These adducts also form complexes with Ni(II) and Zn(II) which are less stable than Schiff base complexes. These results suggest that cyclic imidazolidine structures are formed. Proton magnetic resonance spectra confirm this conclusion. In the presence of a complexing metal ion and excess glyoxylate, the ring of 2-carboxylate imidazolidine opens up to form a quadridentate ligand. Formation constants for these species are reported.

Investigations underway in this laboratory regarding the kinetic and equilibrium properties of aqueous solutions of Schiff base complexes are extended in this work to diamine systems. The reactions of ethylenediamine (en) and *C,C,C′,C′*-tetramethylethylenediamine (temeen) with glyoxylate (glyox⁻) are reported here.

Glyoxylate was chosen for this initial study of diamine behavior because it reacts rapidly and cleanly with amines in aqueous solution,[2] does not dimerize as does pyruvate,[3] and is less likely to give the problems with insolubility which arise with the aromatic aldehydes.

It had been found earlier[2] that glyoxylate reacts with α-alaninate to form a Schiff base.

$$CH_3CH(NH_2)CO_2^- + HCOCO_2^- \longrightarrow CH_3CH(N{=}CHCO_2^-)CO_2^- + H_2O \quad (1)$$

With glycinate, however, the glyoxylate adduct appears to be extensively hydrated as the carbinolamine.[2]

$$NH_2CH_2CO_2^- + HCOCO_2^- \longrightarrow CH_2(NHCHOHCO_2^-)CO_2^- \quad (2)$$

The diamines can react in similar ways and, because a second primary amine group is available, can also add a second glyoxylate to give a bis Schiff base

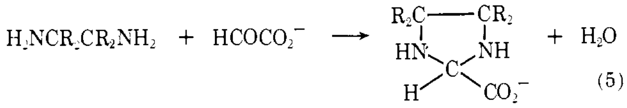
$$NH_2CR_2CR_2N{=}CHCO_2^- + HCOC_2^- \longrightarrow {}^-O_2CCH{=}NCR_2CR_2N{=}CHCO_2^- + H_2O \quad (3)$$

or a bis carbinolamine

$$NH_2CR_2CR_2NHCH(OH)CO_2^- + HCOCO_2^- \longrightarrow {}^-O_2CH(OH)NHCR_2CR_2NHCH(OH)CO_2^- \quad (4)$$

Reactions 3 and 4 yield quadridentate ligands as products, and it was anticipated that the presence of complexing metal ions would promote reactions along these paths.

In addition to the above reactions, cyclic structures may also be formed between polyfunctional amines and carbonyl compounds.[4–8] Pertinent to the present work, cyclization between en or temeen and glyoxylate would lead to an imidazolidine-2-carboxylate.[4]



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The present study was undertaken to determine which of the above diamine–glyoxylate addition reactions are

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