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Dynamic Linkage Isomerization of [3,3'-[Ethylenebis(nitrilomethylidyne)]di-2,4-pentanedionato(2−)]nickel

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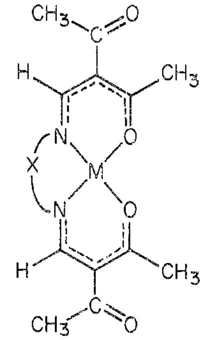
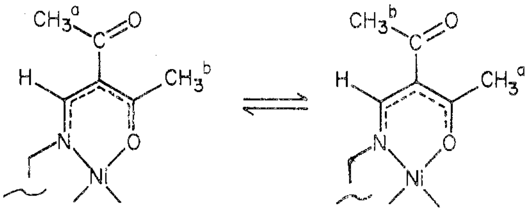
The rate of interchange between coordinated and uncoordinated acetyl groups in the title compound has been measured between 35 and 60°. The interchange (linkage isomerization) was followed by proton magnetic resonance spectroscopy with some of the hydrogens of the uncoordinated acetyl groups replaced by deuteriums for the purpose of "labeling." The process follows first-order kinetics, with rate constant k(at 35°) = $(0.81 \pm 0.05) \times 10^{-4}$ sec^{-1}. The energy of activation for the isomerization is calculated to be 17.4 ± 0.7 kcal mol^{-1} and ΔS^*_{298} to be −20.9 ± 2 eu. It is concluded that a CO group has a significant lifetime coordinated to the nickel(II) ion. The implications of this conclusion which relate to a possible mechanism for reaction of the title compound with amines to give a macrocyclic complex are discussed.

Introduction

Jäger has reported that reactions between complexes containing tetradentate ligands, I, and diamines result in the formation of complexes with macrocyclic ligands.[1] In these systems, the ring-closure process may involve reaction of the amine at the coordinated CO group or at the uncoordinated CO group followed by rearrangement. Alternately, the rate of interchange between the coordinated and uncoordinated CO groups may be sufficiently rapid that they are equivalent and thus it is not possible to determine the position of attack. This interchange process or linkage isomerization may be represented as



I, $X = C_2H_4, C_3H_6, C_6H_4$; M = Ni(II), Cu(II)



In an attempt to draw some conclusions concerning the possible mechanism for the ring-closure process, we have measured the rate of interchange of the "acetyl" groups for I, $X = C_2H_4$ and M = Ni(II), over a range of temperatures from 35 to 60°.

Experimental Section

Preparation of Materials. [3,3'-[Ethylenebis(nitrilomethylidyne)]di-2,4-pentanedionato(2−)]nickel, abbreviated Ni(enp), was prepared as previously reported.[2] The deuterated species, Ni(enp-*d*), was prepared by adding 0.75 g of Ni(enp) to 40 ml of 99% MeOD (Aldrich) and adjusting the pH of the mixture to 12 with NaOH in D_2O. The solution was stirred at 5° for 20 days and filtered, and the residue was dried overnight at room temperature under vacuum over P_4O_{10}.

Procedure for Obtaining Kinetics Data. All proton magnetic resonance (pmr) spectra were obtained with a Varian HA-100 spectrometer. TMS was used as an internal standard and chloroform-*d* used as solvent for recording the complete spectrum at room temperature (see Figure 1). Above room temperature, the spectra were obtained with bromoform as solvent. (No significant solvent effect on the spectrum was observed at room temperature.) Temperature was measured by using an ethylene glycol standard before and after each run. The maximum temperature variation throughout a run is estimated to be ±0.5°.

Table I. Temperature Dependence of the Rate Constants for Linkage Isomerization

Temp, °K	$10^3/T$, °K^{-1}	10^4k, sec^{-1}	Temp, °K	$10^3/T$, °K^{-1}	10^4k, sec^{-1}
308	3.24	0.81 ± 0.05	325	3.08	3.42 ± 0.38
313	3.20	1.20 ± 0.08	329	3.04	4.99 ± 0.44
317	3.15	1.64 ± 0.09	333	3.00	6.0 ± 0.5
320	3.12	2.47 ± 0.17			

A weighed amount of Ni(enp-*d*) was dissolved in a known quantity of bromoform (typical concentrations approximately 5×10^{-2} *M*) and the solution was then transferred to an nmr tube. The tube was capped and placed into the probe which had previously been adjusted to the required temperature. Approximately 5 min was allowed for the sample to reach temperature. The timer was started, and repeated scans of the methyl region of the spectrum from low to high field (δ ~2.5–2.25 ppm) were performed. These scans began ~5 Hz before the low-field peak and continued to ~5 Hz after the high-field peak. Total scan time was approximately 12 sec. For a particular scan, the time was recorded when the recorder pen reached the top of the low-field peak. Repeated scans of the spectrum were obtained until the two peaks were of equal height (see Figure 2). Total run times ranged from ~30 min at 60° to ~2 hr at 35°.

Treatment of Kinetics Data. The heights of the two CH_3 peaks were measured directly from the spectra and the decrease to zero of the peak height difference as a function of time was used for calculation of the kinetics of the interchange process. The data obtained at a particular temperature were treated by KINFIT, a nonlinear curve-fitting program[3] with the Michigan State University CDC 6500 computer. The data fit the expression for a first-order process, *viz.*, $A = A_0e^{-k_{obsd}t}$, where A is the experimental peak height difference at time t, A_0 is the difference at $t = 0$, and k_{obsd} is a first-order rate constant. Variances in the experimental data were also included in the input; variance in t was estimated to be ±1 sec, and in A, ±1 mm. The output includes both the value and the standard deviation of the rate constant. After the treatment of a set of data at a particular temperature by the KINFIT program, those points which deviated considerably from the calculated A *vs.* t curve were dropped from the data and the program was rerun. In no case was there a significant change in the value of k_{obsd} although the standard deviation of k_{obsd} decreased markedly. The rate constant for linkage isomerization, k, is obtained from k_{obsd} by $k = k_{obsd}/2$ (see Discussion). The rate constants k obtained at various temperatures are recorded in Table I. Each value of k is the average of at least two independent runs at the temperature quoted.

Results and Discussion

The 100-MHz pmr spectrum of Ni(enp) in chloroform-*d* at room temperature is shown in Figure 1. The resonance at

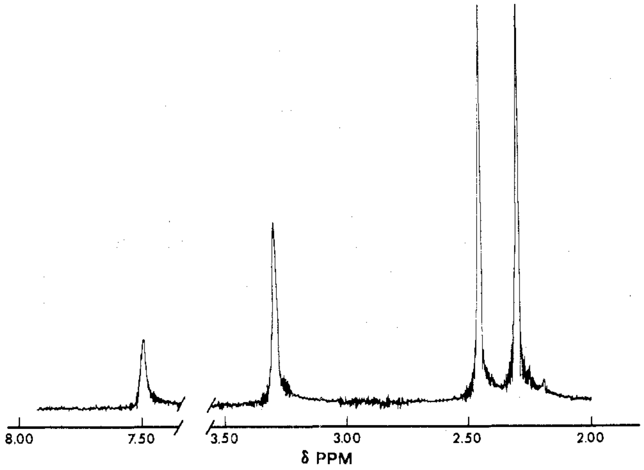


Figure 1. The 100-MHz pmr spectrum of Ni(enp) at room temperature.

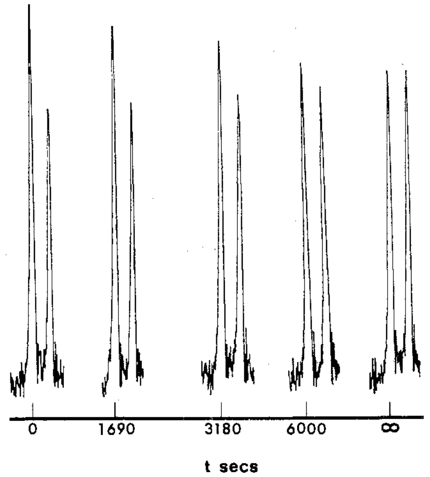
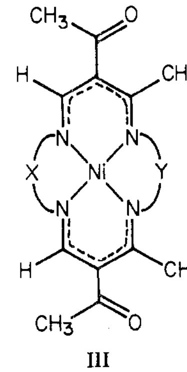
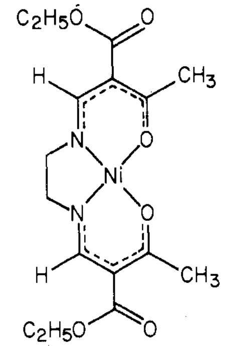


Figure 2. Methyl region of 100-MHz pmr spectrum for Ni(enp-*d*) as linkage isomerization takes place at 40°.

δ 7.49 ppm (relative intensity 2) downfield from the internal TMS standard is assigned to the hydrogens attached to the six-membered chelate rings of the ligand in Ni(enp), I, X = C_2H_4, and the resonance at δ 3.30 ppm (relative intensity 4) is assigned to the methylene hydrogens. The two remaining resonances (each of relative intensity 6) at δ 2.29 and 2.44 ppm are assigned to the hydrogens of the uncoordinated and coordinated CH_3CO groups, respectively. Recently, Hipp and Busch[4] reported pmr spectra of some nickel(II) complexes with macrocyclic ligands which contain uncoordinated CH_3CO groups in the γ (or 3) position of the six-membered chelate ring, III. Resonances in the range δ 2.27–2.30 were assigned to the hydrogens of the uncoordinated CH_3CO groups whereas those in the region of δ 2.4 ppm were assigned to the hydrogens of the methyl groups directly attached to the macrocyclic ligand. In the nickel(II) complex IV and the macrocyclic complex derived from it by condensation with ethylenediamine, the methyl hydrogens are observed as a singlet at 2.40 ppm,[5] close to the position observed for the hydrogens of the coordinated CH_3CO group in Ni(enp). The pmr spectrum of Ni(enp) remains unchanged in $CHBr_3$ up to 110°, above which temperature decomposition takes place. Since there is no evidence for line broadening and the methyl hydrogens remain distinguishable in the two different environments even at elevated temperatures, linkage isomerization is not occurring rapidly, *i.e.*, on an nmr time scale. In $M(triac)_3$ complexes (M = Al, Ga; triac = 3-acetylpentane-2,4-dionato), line broadening was not detected up to 180° and it was concluded that linkage isomerization is not a rapid process in these species.[6]

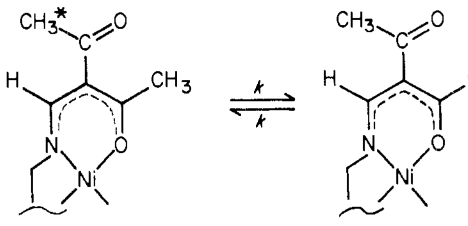


III



IV

In order to measure the rate of linkage isomerization for Ni(enp), the methyl groups in the different environments were made identifiable by means of selective deuteration. Suspension of Ni(enp) in basic MeOD at 0–5° effects deuteration of the high-field methyl hydrogens, *i.e.*, those of the uncoordinated CH_3CO groups. Under these conditions, which give maximum selective deuteration, approximately 30% of the hydrogens of the uncoordinated CH_3CO groups are deuterated whereas no other hydrogens of the ligand are deuterated. The use of longer times and/or higher temperatures for the deuteration process results in less selectivity and ultimately in complete deuteration of all the methyl hydrogens. The linkage isomerization was followed by monitoring the difference in peak heights for the methyl hydrogens in the partially deuterated sample Ni(enp-*d*) as it decreased to zero. At no temperature was the total amount of deuteration decreased, ruling out any exchange with the solvent, nor was there any evidence for exchange between added ligand and coordinated ligand. Figure 2 shows the methyl region of the pmr spectrum at various times at 40° for the isomerization (where the asterisk signifies labeling by deuterium)



L M

For linkage isomerization

$$\frac{d(L)}{dt} = -k[(L) - (M)] \qquad \text{EQU A}$$

and

$$\frac{d(M)}{dt} = k[(L) - (M)] \qquad \text{EQU B}$$

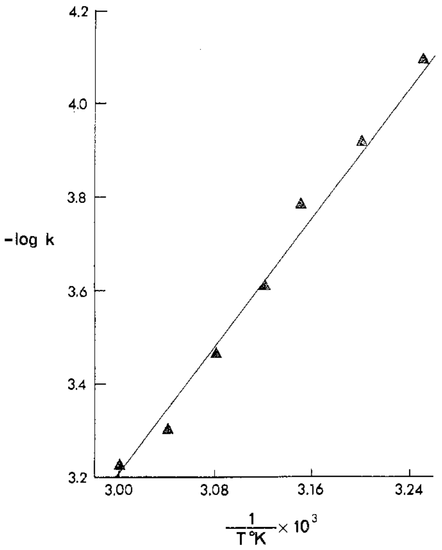


Figure 3. Plot of log k *vs.* $1/T°$K for linkage isomerization.

Now, A the experimental peak height difference is proportional to [(L) − (M)]. Thus

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\mathrm{d}[(\mathrm{L}) - (\mathrm{M})]}{\mathrm{d}t} = -2k[(\mathrm{L}) - (\mathrm{M})] = -2kA$$

i.e.

$$\mathrm{d}A/A = 2k\mathrm{d}t$$

$$\ln A = -2kt + \ln A_0 \qquad A = A_0e^{-2kt}$$

In the Experimental Section, the expression $A = A_0e^{-k_{\mathrm{obsd}}t}$ was used for treatment of the data. Thus $k = k_{\mathrm{obsd}}/2$.

The data obtained for the isomerization were treated as described in the Experimental Section. The isomerization is a first-order process and values of the first-order rate constants, k, obtained over the temperature range 35–60° are listed in Table I. A plot of log k *vs.* $1/T°$K is shown in Figure 3. From this plot, the energy of activation for the isomerization, E_a, is calculated to be 17.4 ± 0.7 kcal mol^{-1}, and log A, 8.24. From the log A value, ΔS^*_{298} is calculated to be −20.9 ± 2 eu. The fairly high negative value of ΔS^*_{298} indicates that a symmetric intermediate is produced in the linkage isomerization process, which involves rotation about a $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ bond of the ligand. We suggest that, in this symmetric intermediate, "coordination" of both oxygens to the nickel(II) occurs.

Fay[7] has observed linkage isomerization of triac in Co(triac)$_3$ and Co(acac)$_2$(triac). He obtained E_a and ΔS^*_{298} values of 39.6 ± 1.6 kcal mol^{-1} and 28 ± 4 eu and 39.9 ± 1.8 kcal mol^{-1} and 28 ± 5 eu, respectively. In these cobalt complexes, the linkage isomerization is proposed to proceed *via* a five-coordinate intermediate produced by Co—O bond rupture followed by rotation about a $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ bond within the resulting unidentate ligand and Co—O formation. This mechanism is consistent with the observation of a large positive value for ΔS^*_{298}. The cobalt(III) ion is six-coordinated in these complexes and a mechanism involving reduction of the coordination number of the cobalt(III) ion is reasonable for the linkage isomerization. However, for Ni(enp), the nickel(II) ion is four-coordinated and a mechanism invoking association of both CO groups with the nickel(II) ion during the isomerization both is plausible and is in agreement with the observed negative value for ΔS^*_{298}.

The preexchange lifetime, τ, *i.e.* the lifetime of a particular configuration prior to the isomerization taking place, can be obtained from the rate constant by $\tau = 1/k$. For Ni(enp-*d*) in bromoform, τ varies from 12.4 × 10^3 sec at 35° to 1.66 × 10^3 sec at 60°. From this information, it is possible to draw some conclusions concerning the ring-closure reaction of Ni(enp) with amines. Reactions of CO groups with amines proceed *via* nucleophilic attack of the amine at the carbon atom of the CO group. In Ni(enp), there are two potential reaction sites, the carbon of the coordinated acetyl group and that of the uncoordinated acetyl group. Since the linkage isomerization is slow and a particular configuration of the ligand has a significant preexchange lifetime, the nickel(II) ion will have a significant effect on the electron density within the ligand. Coordination will result in decreased electron density at the carbon of the coordinated CO group. The uncoordinated acetyl group may also reduce electron density at the carbon of the coordinated CO group due to its electron-withdrawing nature. Thus the carbon atom of the coordinated CO will be the preferred site for nucleophilic attack by amines in the ring-closure process. Attempts to confirm this conclusion by reaction of Ni(enp-*d*) with amines were not successful however, since very rapid exchange of the deuteriums of the uncoordinated acetyl groups occurred in the presence of amines and the macrocycle obtained was nondeuterated.

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Registry No. Ni(enp), 53385-23-2.

References and Notes

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