

## Effect of Pressure on the Nitro–Nitrito Linkage Isomerism in Solid $\text{Ni}(\text{en})_2(\text{NO}_2)_2^*$

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Linkage isomerism in nickel complexes of the type  $\text{NiL}_2(\text{NO}_2)_2$ , where  $\text{L} = \text{RR}'\text{N}-\text{CH}_2-\text{CH}_2-\text{NR}''-\text{R}'''$ , has been very well characterized [1–6]. The equilibrium between the nitrito and nitro isomers has been studied primarily in solution, and to a large extent by spectroscopic techniques. In solution studies the nitrito–nitro equilibrium has been found to be strongly pressure-dependent, the nitro specie being favored by pressure [6]. In the case of the ethylenediamine (en) complex, the red dinitro isomer is stable at room temperature, while the violet form is formed at higher temperature [4]. It has been determined that the nitro complex possesses the higher density and therefore the smaller molecular volume [3], and would be the pressure stable phase. It has also been found that steric effects play an important role in the stabilization of a particular isomer [2, 4, 5]. For example, in complexes involving bulky, substituted diamine complexes the nitrito form may be more stable [2, 4, 5]. Little is known of the effect of pressure on the nitrito–nitro ligand isomerism in the solid state. Since steric effects should play only a minimal role in en complexes, we have chosen to study the effects of pressure on  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$ , using optical probes to identify the pressure-stable isomer. Furthermore, thermal behavior of the complex has been investigated by a scanning calorimetric technique in order to evaluate the energy difference between the two isomers. This paper reports on the results of this investigation.

### Experimental

The complex was prepared according to methods previously described [4]. Electronic spectra were recorded in a diamond anvil cell (DAC) [7] using a

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Cary 14 spectrophotometer interfaced with a special beam condenser [8]. The spectra at elevated temperatures were measured with a DAC equipped with a heating element surrounding the diamonds. Temperature was measured with a chromel–alumel thermocouple using an ice bath junction as reference. The thermal behavior was studied by a quantitative thermal analysis technique using the Mettler TA 2000 apparatus, calibrated for temperature and enthalpy changes as previously described [9].

### Results and Discussion

The  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$  complex is red colored at room temperature, and becomes violet at  $\sim 120^\circ\text{C}$ . The red isomer corresponds to the dinitro form, while the violet form is the dinitrito form [3]. The nitro form has absorption maxima at  $\sim 560$  and  $\sim 800$  nm, and these shift to about 560 and 900 nm when the nitrito isomer is formed. Figure 1 demonstrates the absorption spectra ( $\sim 800$  nm band) of the nitro form as a function of temperature. The shift of the absorption band with temperature, corresponding to a conversion of nitro to nitrito isomer, appears to be slight until one reaches  $\sim 112^\circ\text{C}$ . Once formed, the violet, nitrito form can be maintained for several hours. These measurements were recorded using a DAC, and increases in temperature and/or pressure will cause extrusion of material in the cell, and thinning of the sample results. This makes optical measurements more difficult, particularly for substances having small absorption coefficients.

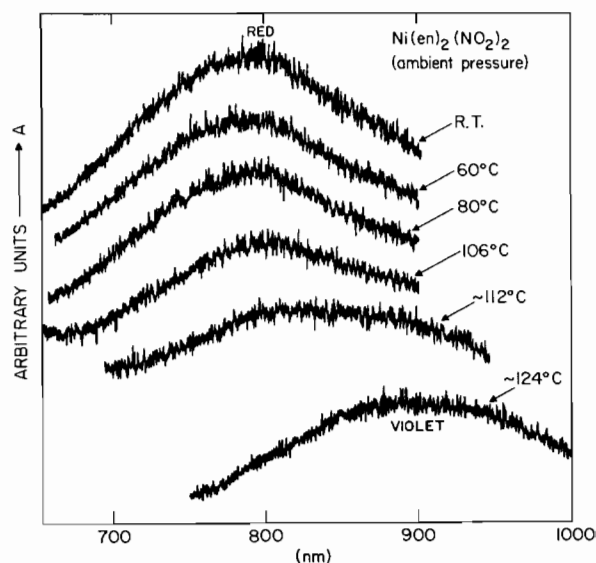


Figure 1. Effect of temperature on the 800 nm absorption of  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$ .

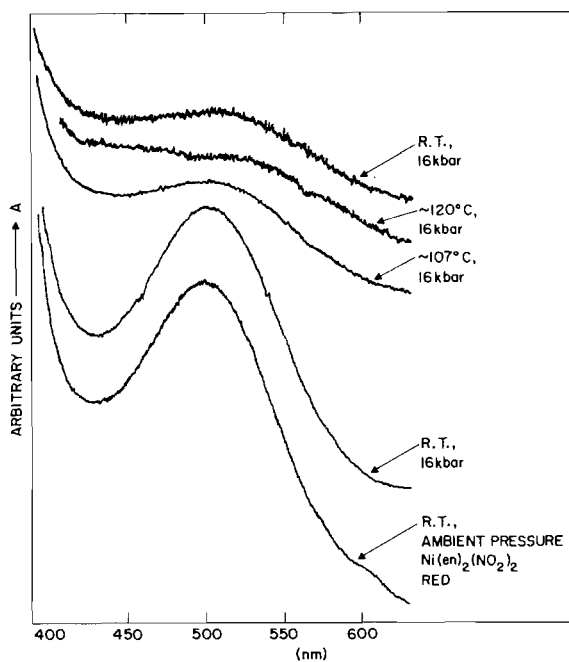


Figure 2. Effect of pressure on the nitro form of  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$ , at room temperature and at elevated temperatures.

The nitro form is presumed to have the smaller volume and should be the pressure-stable form [3]. Figure 2 shows the effects of pressure on the nitro isomer using the  $\sim 500$  nm absorption band as the diagnostic probe. It may be observed that this isomer remains unchanged with pressure even when the sample is heated to  $\sim 120^\circ\text{C}$ , the temperature at which the nitrito isomer should be the stable form. Figure 3 illustrates the conversion of the nitrito form to the nitro form with pressure. The  $560$  nm absorption is observed to shift toward lower frequency to  $\sim 500$  nm as the pressure is increased, maintaining the temperature at  $\sim 126^\circ\text{C}$ . The shift with pressure is gradual, and may reflect the omnipresent pressure gradient existing in the DAC when it is used without a gasket and in the absence of a transmission fluid. The band at  $\sim 900$  nm was not followed with pressure because of the inherent weak absorption of this band.

Although the nitro form may involve a smaller volume, it has been predicted to have greater steric hindrance than the nitrito form, especially in complexes containing substituted ethylenediamine ligands [2]. The conversion with pressure of the nitrito isomer of  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$  to the nitro isomer form in the solid state overcomes any steric effects, as well as lattice constraints. The complex  $\text{Ni}(\text{N,N}'\text{-di(en)})_2(\text{NO}_2)_2$ , which at room temperature is in the dinitrito form (blue), remains unchanged with pressure to  $\sim 75$  kbar. This complex demonstrates considerable steric hindrance [2] between anion and diamine as the anion approaches the metal in the axial positions, and these steric effects are not overcome with pressure.

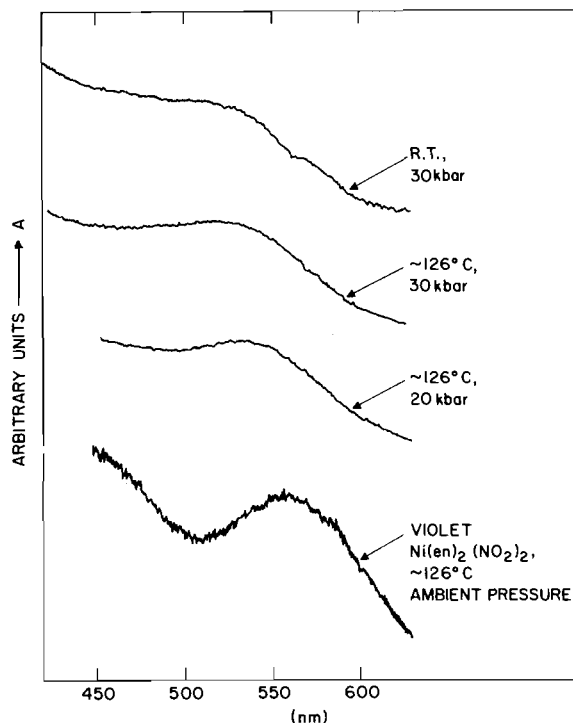
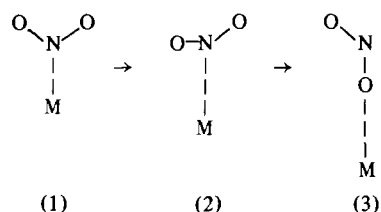


Figure 3. Effect of pressure on the nitrito form of  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$ .

Calorimetric analysis of the red form provided evidence for an endothermic transition beginning at  $98\text{--}100^\circ\text{C}$ , and which is complete at  $\sim 116^\circ\text{C}$  (at a heating rate of  $2$  to  $4^\circ\text{C}/\text{min}$ ). At the end of the transition the compound is found to be violet. The large temperature interval, in comparison with those observed for analogous endothermic rearrangements of some other nickel(II) bis-diamine complexes [9], suggests the existence of a large kinetic barrier for interconversion. The absorbed energy is found to be  $1.47 \pm 0.07$  kcal/mol $^{-1}$ , and it is not restored on quick cooling. However, the same sample, kept in a desiccator at room temperature for several hours, recovers its pristine red color, and when heated on the calorimeter, gives an endothermic peak of the same area at the same temperature interval as previously.

Results obtained spectroscopically and calorimetrically may be reconciled by the possibility of a transition state existing between the nitro and nitrito states, such as is illustrated as follows:



State (2) may absorb similarly to state (1), and may account for the results in Fig. 1, where there is an unnoticeable change from room temperature to 106 °C. Only when the anions have become coordinated through the oxygen atoms (state (3)) at ~120 °C does the absorption correspond to the violet, nitrito form.

From a statistical point-of-view it can be seen that the nitro to nitrito interconversion is favored by an increase in entropy. In the nitro form only one atom (nitrogen) can coordinate to the metal ion. On the other hand, in the nitrito form the coordination can occur at one or another equivalent oxygen atom. At 100 °C the interconversion of nitro to nitrito, in the title complex under investigation, is displaced toward the nitrito isomer by a favorable entropy change ( $\Delta S^\circ = 4 \text{ cal K}^{-1} \text{ mol}^{-1}$ ). The statistically predicted  $\Delta S^\circ$  is less ( $2R \ln 2 - R \ln 1 = 2.7 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) than the experimental value. The excess entropy can be ascribed to an increase in configurational entropy of the coordinated diamine due to the diminishing steric hindrance from the apical anions.

### Conclusions

(1) It has been demonstrated that application of pressure can convert the nitrito isomer of  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$  to the nitro form in the solid state, overcoming any steric effects and lattice forces present in the complex.

(2) The interconversion of nitro to nitrito is endothermic ( $\Delta H^\circ = 1.47 \pm 0.07 \text{ kcal/mol}^{-1}$ ), and at the transition temperature as shifted toward the nitrito form by the favorable entropy change ( $\Delta S^\circ = 4 \text{ cal K}^{-1} \text{ mol}^{-1}$ ).

(3) The complex  $\text{Ni}(\text{N,N}'\text{-dieten})_2(\text{NO}_2)_2$  in the nitrito form, where larger steric factors are involved, does not convert to the nitro isomer up to ~75 kbar.

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