there is a preceding conformational change to give the i,o complex (or the o,o) which leaves one of the lone pairs on nitrogen free to be trapped by H^+.

$$\begin{tikzcd} \text{i,i}\,(M^{n+}) \arrow[r, shift left, "K_{\text{conf}}"] & \text{i,o}\,(M^{n+}) \arrow[l, shift left] \arrow[r, shift left, "K_{H^+}"] \arrow[d, "k_1"] & \text{i,o}\,(M^{n+}, H^+) \arrow[l, shift left] \arrow[d, "k_2"] \\ & (\text{i,o}) + M^{n+} & \text{i,o}\,(H^+) + M^{n+} \end{tikzcd}$$

A possible kinetic scheme for the dissociation reaction is shown below. The scheme as written assumes that the slow steps in the process are the dissociation of the metal from the protonated and free i,o cryptates in the catalyzed and uncatalyzed paths, respectively. Under these conditions, the rate constant for the uncatalyzed dissociation would equal k_1K_{conf}, which would explain the slow dissociation rates observed for the cryptates if K_{conf} is small, i.e., i,i is the dominant conformation at equilibrium. There are, however, a number of other possibilities within the same general kinetic scheme. For example, the slow step in the acid catalyzed pathway could be the protonation of the cryptate (followed by rapid dissociation of the protonated cryptate).

A further point of interest in the present results concerns the relative magnitudes of the catalyzed and uncatalyzed rates and, in particular, the fact that some of the dissociation rates are apparently independent of the acid concentration. Such a result would be obtained if the conformational change i,i (M^{n+}) to i,o (M^{n+}) were rate determining—the acid could then only affect the rates of steps subsequent to the rate determining step. A rate determining conformational change has previously been suggested to account for the observed kinetic behavior in the Ca^{2+} antamanide system.[11] Further discussion of this point will be deferred until a more systematic study of cryptates is completed. It is, however, noticeable that within the alkaline earth series, the ratio k_{H^+}/k_d increases considerably as the cryptand varies from 2,1,1 to 2,2,1 and 2,2,2, and is not smallest for the most stable cryptate, or the one having the lowest dissociation rate.

A final account of this work will include, in addition to results at 25 °C for a wider range of cryptates, activation parameters for the dissociation rates, to be combined with currently available enthalpies and entropies of reaction.[3,4]

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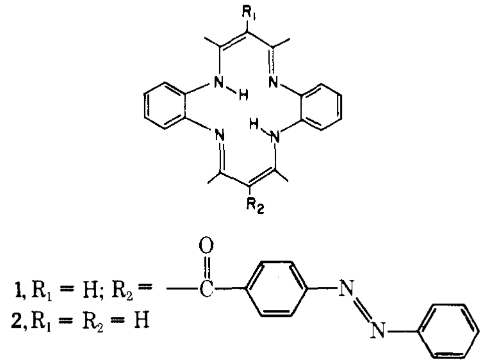
Macrocyclic Schiff Base Complexes Bearing Photoactive Substituent Groups. 1. The Azo Linkage

Sir:

It has long been recognized that certain organic molecules which undergo photoisomerization reactions exhibit a form of photoenergy conversion and storage.[1] In these systems a photoreaction is responsible for converting the most stable form of the compound into a thermodynamically unstable isomer. Since the isomerization of the higher energy isomer back to the more stable form is exothermic, the system has the effect of converting light energy into heat energy.

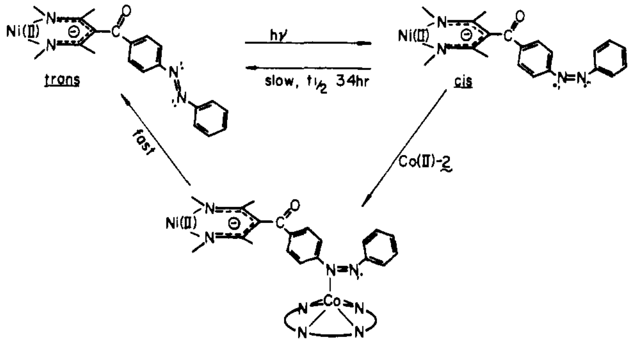
Numerous organic compounds undergo photoisomerization reactions. Azo compounds, various stilbenes, and acyclic Schiff bases and their analogues are subject to a photoisomerization about a double bond.[2] Since the separation is energy between the more stable trans and the less stable cis form is small for these compounds (3-5 kcal/mol) the energy storage capacity of the system is modest. On the other hand, for organic molecules which exhibit a photodriven bond isomerization reaction, e.g., norbornadiene and anthracene, the storage capacity can be high (~30 kcal/mol).[3] Solar energy storage systems involving bond isomerization reactions are currently being investigated as practical sources of "low grade" heat.[3,4]

Certain metalloporphyrin compounds have been successfully used as sensitizers for photoisomerization reactions.[5] However, the ability of structurally related macrocyclic Schiff base complexes to assist in photoenergy transfer and storage phenomena has not been explored. In an effort to examine the usefulness of these cyclic structures in a photoenergy storage cycle we have synthesized the macrocyclic ligand **1**, from the parent Schiff base **2**. We have found that the nickel complex of **1**, Ni(II)-**1**, undergoes a photoisomerization about the azo linkage to give the less stable cis azo isomer. We have further demonstrated that the photogenerated cis isomer is capable of bonding to a second metallomacrocyclic complex and in so doing is catalytically reisomerized to the trans form (Scheme I). Since the reisomerization is accompanied by the release of heat, the system has the effect of converting photoenergy into heat energy.



1, R_1 = H; R_2 =
2, R_1 = R_2 = H

Scheme I



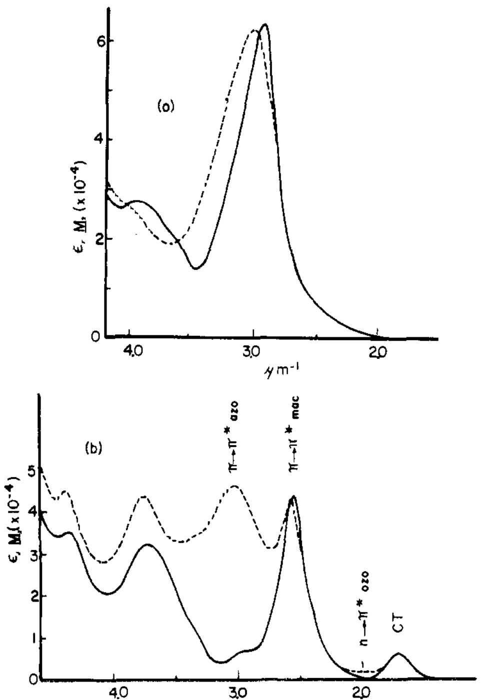


Figure 1. (a) The absorption spectra of **1** (- - -) and **2** (—) in CH_3CN are shown. (b) The absorption spectra of Ni(II)-**2** (—) and Ni(II)-**1** (- - -) in CH_3CN are shown.

The reaction of *p*-phenylazobenzoyl chloride with **2**[6] in a 1:5 molar ratio yields the deep red crystalline solid **1**.[7] The free ligand **1** reacts with transition metal ions and in the presence of excess $Ni^{II}(CH_3CN)_6(BF_4)_2$[8] and triethylamine in acetonitrile as a solvent readily forms Ni(II)-**1**. The UV-visible spectrum of the azo ligand, Figure 1a, exhibits a band at 3.01 μm^{-1} (ϵ 62 700) which contains at least two absorption envelopes. One is due to a $\pi \rightarrow \pi^*$ transition of the cyclic Schiff base framework while the second is associated with a $\pi \rightarrow \pi^*$ transition of the trans form of the azo chromophore. The cis form of azobenzene and its analogues have substantially different absorption maxima and intensities and as such are easily detected via optical techniques.[9] Comparison of the absorption spectrum of Ni(II)-**1** with that of Ni(II)-**2**,[10] Figure 1b, allows the assignment of the strong band (ϵ 3.9 × 10^4) at 3.05 μm^{-1} to the $\pi \rightarrow \pi^*$ transition of the trans form of the azo chromophore. The $n \rightarrow \pi^*$ transition of the azo linkage is weaker and occurs at the visible absorption minimum (~2.00 μm^{-1}) in the spectrum of Ni(II)-**1**. On the basis of extensive resonance Raman investigations on Ni(II)-**2**[10] the visible band at 1.72 μm^{-1} (ϵ 6.8 × 10^3) for both Ni(II)-**1,2** can be assigned to a charge transfer transition. These same investigations have revealed that the strong band at 2.58 μm^{-1} (ϵ 4.8 × 10^4) for Ni(II)-**1,2** is due to a $\pi \rightarrow \pi^*$ electronic transition of the macrocyclic framework. From these observations it is clear that the spectrum of Ni(II)-**1** is a simple superposition of that found for Ni(II)-**2** and a 4-substituted azobenzene.[2] Thus, the two chromophores although joined in Ni(II)-**1** do not or at most only weakly interact with each other.

Irradiation of solutions containing Ni(II)-**1** with an argon ion laser at 5017 Å (1.9932 μm^{-1}), which is essentially into the $n \rightarrow \pi^*$ transition of the azo chromophore, resulted in a spectral change.[11] The difference spectrum of Ni(II)-**1** as a function of time after irradiation is shown in Figure 2. The bands are 4.10, 3.59, and 2.28 μm^{-1} (Figure 2) are in excellent agreement with those for the cis form of azobenzene itself (4.13, 3.57, and 2.31 μm^{-1})[9] and must be due to the cis form of Ni(II)-**1**. As a check, a portion of the irradiated solution was analyzed using thin layer chromatography. Only two components were found, the major of which corresponded to trans Ni(II)-**1** (identified by its absorption spectrum, Figure 1b, and a spot of weaker intensity which proved to be cis Ni(II)-**1**.[12] In acetonitrile solution pure cis Ni(II)-**1** slowly reverts back to trans Ni(II)-**1** at the same rate as that observed for the collapse of the difference spectrum (Figure 2) back to the baseline. The observed first-order rate constant for the process was 5.6 × 10^{-6} s^{-1}.[13]

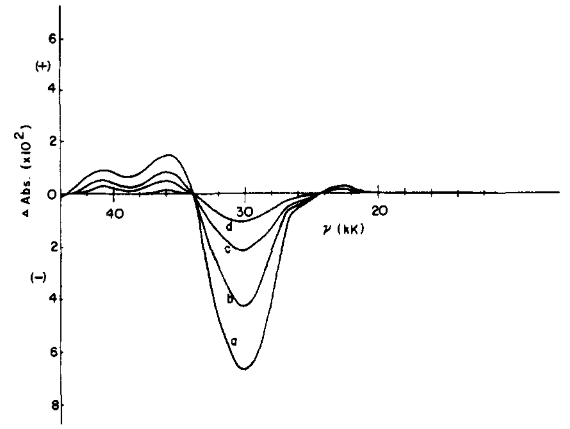


Figure 2. The difference spectrum of a 1.4 × 10^{-5} M acetonitrile solution of Ni(II)-**1** at various times after irradiation is shown: (a) immediately after irradiation, (b) 24 h, (c) 67 h, (d) 118 h. Conditions of irradiation are as described in footnote 11. (1 kK = 0.1 μm^{-1}.)

In an attempt to affect the isomerization via one of the transitions associated with the macrocyclic chromophore, the charge transfer band at 1.72 μm^{-1} was irradiated (specifically with 5909 Å, 1.6923 μm^{-1} radiation). Unlike a number of Ru(II)-stibazole complexes which do exhibit intramolecular energy transfer phenomena,[14] irradiation of the CT band of either trans or cis Ni(II)-**1** did not yield the isomerization. Although more detailed investigations are required, the inactivity of the CT band in Ni(II)-**1** may be related to the presence of a number of accessible low lying d-d excited states for the diamagnetic d^8 ion. A similar argument has been advanced to explain the observed lack of emission in Ni(II) porphyrin complexes.[15]

In an effort to prevent the slow exothermic isomerization of cis Ni(II)-**1** to trans Ni(II)-**1** and thus permanently store the energy present in the cis form of the dye, we examined the coordinating ability of cis and trans Ni(II)-**1**, *cis*- and *trans*-azobenzene, and various other azo chromophores with Co(II)-**2**.[10,16] Similar to numerous Co(II)-porphyrin compounds,[17] this Schiff base analogue, Co(II)-**2**, forms stable axial adducts with nitrogen donor ligands such as pyridine and pyperidine. However, attempts to coordinate either cis or trans Ni(II)-**1** or the azobenzene isomers to the cobalt complex were unsuccessful. ESR spectra (80 K, X band) of toluene glasses containing the cobalt complexes and the various cis and trans isomers gave only the spectrum characteristic of the four-coordinate square planar cobalt compound ($g_z = g_y = 1.7$, $g_x = 3.83$, a^{Co} 2.74 × 10^{-2} cm^{-1}). A check of the absorption spectrum of the solution containing the cis isomers (cis Ni(II)-**1** and *cis*-azobenzene) and the Co(II) complex revealed that the azo compounds had rapidly and quantitatively isomerized to the trans forms. This catalytic behavior on the isomerization rate of azobenzene is not common but has been noted in at least one other case.[18] As a check on the ability of the cobalt complex to bind a cis azo group, the ESR spectrum of a solution containing Co(II)-**2** and a tenfold molar excess of 2,3 diazo bicyclo[2.2.1]hepta-2-ene,[19] was determined. This compound possesses an azo linkage in the cis geometry which is not free to isomerize. The ESR data indicated that the azo bicyclic compound readily binds to Co(II)-**2**. The observed ESR transitions were: toluene (80 K), $g_x = 2.38$, $g_y = 2.24$, $g_z = 2.00$; $a^{Co} = 105$ G, 97.7×10^{-4} cm^{-1}; $a^{N} = 20$ G, 18.7×10^{-4} cm^{-1}. Particularly informative is the appearance of only three superhyperfine lines on the high field ESR transition indicating that only one nitrogen atom binds to the Co(II) ion. Thus, facile isomerization of the cis isomers in the presence of Co(II)-**2** is probably due to the formation of a dπ-pπ bond between the metal ion and the bound nitrogen atom. Electronic delocalization of this type would have the effect of reducing the double bond character of the azo linkage itself and thus facilitate the isomerization to the stable trans isomer.

Finally, a toluene solution containing 1.4 μM Co(II)-**2** and 14 μM trans Ni(II)-**1** was irradiated as before using 5017 Å radiation.[20] The fact that no isomerization was observed under these conditions taken with the ESR results is supportive of the energy releasing process shown in Scheme I. Thus, the photoreaction transforms a sterically incumbered ligand, trans Ni(II)-**1,** into a good donor group, cis Ni(II)-**1** which subsequently binds to Co(II)-**2.** This bis macrocyclic complex is unstable and rapidly decomposes to give trans Ni(II)-**1,** Co(II)-**2,** and heat. All efforts to trap and examine the unusual intermediate bis macrocyclic complex have been unsuccessful to date.[21]

The overall efficiency of converting photoenergy into thermoenergy for the system described in this report is low.[22] However, since the metallomacrocyclic framework gives rise to strong metal dependent absorptions in the visible region, the compounds can be viewed as polychromic absorbers. The combination of this feature with the ability to attach other higher energy acceptor molecules to the macrocyclic framework enhances the possibility of using this type of macrocyclic structure in an efficient photo-thermo conversion process. We are continuing to study the forward light driven reaction as a function of both the coordinated metal ion and the structure of the covalently bound acceptor molecule. At the same time the effects of various chemical agents on the energy releasing step are being explored.

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(7) The compounds **1** (52% yield) and Ni(II)–**1** (60% yield) gave acceptable analytical and mass spectral data: *m/e*, calcd (obsd), **1,** 553 (553); Ni(II)–**1** 609 (609). ^{1}H (NMR) (CDCl$_3$), **1** δ 2.02 (s, 6 H), 2.17 (s, 6 H), 4.90 (s, 1 H), 7.0–8.3 (m, 17 H) 12.25 (s, 1 H), 13.88 (s, 1 H); Ni(II)–**1** δ 1.83 (s, 6 H), 2.05 (s, 6 H), 4.83 (s, 1 H), 6.5–8.5 (m, 17 H).

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(11) All irradiation experiments were done using a Spectra Physics Model 166-03 argon ion laser with a Spectra Physics Model 375 dye laser for the long wavelength studies. The solutions, which were run in duplicate, were thoroughly degassed before irradiating. Typical irradiation conditions employed a laser intensity of about 20 mW for durations of under 2 min. Using these conditions no degrading of the compound in solution could be observed. Longer irradiation times and higher powers lead to some decomposition as evidenced by the inability of the irradiated solution to completely return to its original spectral properties. The observed quantum yields were referenced against a ferric oxalate actiometer; C. A. Parker, "Photoluminescence of Solutions", Elsevier, New York, N.Y., 1968, p 208. Difference spectral techniques were used to measure the amount of cis Ni(II)–**1** present after irradiation. The quantum yield value was obtained on solutions containing <3% of cis Ni(II)–**1** Φ_{5017} trans → cis 3.3×10^{-2}; pps 76% trans.

(12) Thin layer conditions. Silica gel (C$_6$H$_6$); R_f trans Ni(II)–**1** 0.55, cis Ni(II)–**1** 0.25.

(13) The first-order rate constant for the cis to trans isomerization of azobenzene is 1.6×10^{-6} s^{-1}; R. J. W. LeFevre and J. Northcott, *J. Chem. Soc.*, 867 (1953).

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(19) *Org. Syn.*, *V*, 97.

(20) Although Co(II)–**2** is an intensely absorbing compound this ratio of the complexes produces an absorption spectrum essentially identical with that shown in Figure 1b.

(21) Irradiation of toluene glasses (80 K) containing Co(II)–**2** and trans Ni(II)–**1** have not yielded the five-coordinate Co(II)–**2**, cis Ni(II)–**1** adduct. The ESR parameters of such an irradiated glass are identical with those described in the text for Co(II)–**2** in toluene.

(22) At 5017 Å only about 0.1% of the energy input is returned as heat. The low efficiency is directly attributable to both the nonsensitized nature of the light driven photoreaction and the low thermo yield of the cis–trans azo isomerization.

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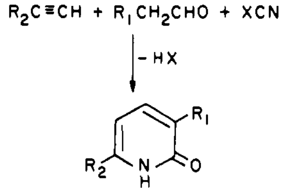
A New Synthesis of 2-Pyridones. Solution Thermolysis of Propargylic Pseudoureas

Sir:

The 2-pyridone ring is an important structural feature of a number of natural alkaloids,[1,2] and several pharmacologically active series of compounds.[3] In this communication we report an experimentally simple, and mechanistically novel, new synthesis of substituted 2-pyridones. The formal construction of the 2-pyridone ring which is possible by this new methodology is illustrated below. The highly convergent nature of this approach and the availability of the precursor components[4] are features which make this a noteworthy addition to existing methodology.[5]



The approach is illustrated in Scheme I. Base catalyzed condensation[6] of secondary propargylic alcohols and 1-cyanopyrrolidine[7] at 0–25 °C produced pseudoureas **1** in yields (crude) in excess of 85%. These intermediates were not puri-

Scheme I