Communications to the Editor

Photochemical Perturbation and Chemical Relaxation of the Planar — Tetrahedral Equilibrium in a Di(tertiary phosphine) Complex of Nickel(II)

Sir:

Tetrahedral — square-planar isomerization in nickel(II) complexes is an established phenomenon. The thermodynamics and, to a more limited extent, the kinetics have been investigated by NMR.[1] We now wish to report our observations on a system where the isomerization can be effected *photochemically* by a Q-switched laser pulse. As well as offering a rather novel technique for studying the kinetics of isomerization, the observations are of interest with regard to the possible importance of excited state distortions in the photochemistry of transition metal complexes.[2] This is also the first documented[3] report of ligand-field photochemical activity in tetrahedral or planar complexes of nickel(II).

The system we have studied is the complex dichloro-1,3-bis(diphenylphosphino)propanenickel(II) (abbreviated Ni(dpp)Cl_2), in dichloromethane or acetonitrile as solvent. A planar $\rightleftharpoons$ tetrahedral equilibrium in this system was first reported and the thermodynamics were investigated by Van Hecke and Horrocks.[4]

Solutions of the complex ((0.7–1.4) $\times$ 10^{-3} mol dm^{-3}) were irradiated with a Q-switched pulse (0.1–0.4 J) from a neodymium laser at either the fundamental wavelength (1060 nm) or the second harmonic (530 nm), generated by means of a phase-matching ADP crystal. The rapid changes in absorbance which resulted were monitored in the wavelength range 375–530 nm. Figure 1 presents the significant observations.

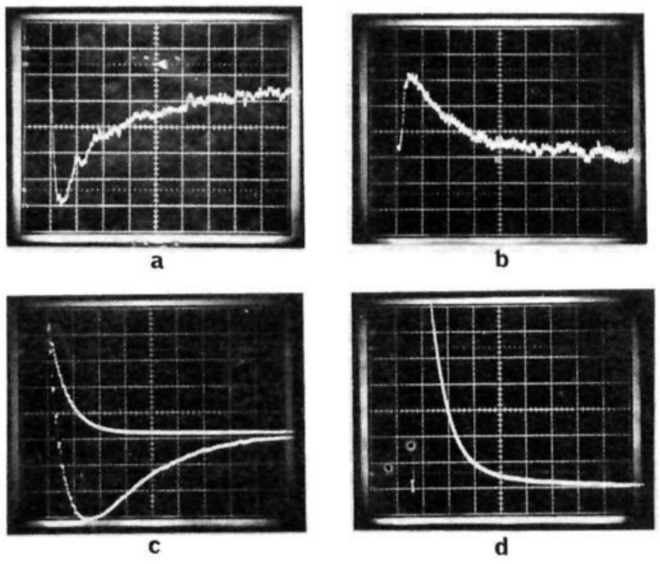

Figure 1. Absorbance changes as a function of time in $\sim 10^{-3}$ mol dm^{-3} Ni(dpp)Cl_2 solutions (absorbance increasing downwards in all cases): (a) irradiation wavelength 1060 nm; monitoring wavelength 470 nm; vertical scale, 1% absorbance change/division; horizontal scale, 0.5 μsec/division; temp 23°; (b) irradiation 1060 nm; monitoring 380 nm; vertical scale, 0.3% absorbance change/division; horizontal scale, 0.5 μsec/division; temp 21°; (c) (lower trace) irradiation 530 nm; monitoring 400 nm; vertical scale, 10 mV/division; horizontal scale, 0.5 μsec/division; temp 24.5° (*Upper trace*) scattered laser pulse; (d) irradiation 530 nm; monitoring 475 nm; vertical scale, 50 mV/division; horizontal scale, 0.5 μsec/division; temp 23°. Solvent in d is CH_2Cl_2; others are CH_3CN.

Irradiation at 1060 nm resulted in a rapid increase and subsequent decay in the absorbance at wavelengths in the range 450–530 nm, where absorption is largely due to the planar isomer[4] (Figure 1a). Similar effects were seen by monitoring at shorter wavelengths (375–430 nm) except that the reestablishment of equilibrium was preceded by a *decrease* in absorbance (Figure 1b). Significantly, however, at all monitoring wavelengths the reestablishment of equilibrium proceeded with the same time constant (0.93 ± 0.04 μsec at 23°). At 1060 nm, the absorbing species is the tetrahedral isomer[5,6] and the initial increase in absorbance, in the range 450–530 nm, following irradiation marks the rapid formation of the planar isomer. According to this interpretation, the concomitant depletion of the tetrahedral ground state within the laser pulse should also be observable and this is shown in Figure 1b. The monitoring wavelength in this case is in the charge-transfer (CT) region but it is reasonable to expect that the CT absorption intensity would be higher for the tetrahedral than for the planar isomer.[7] When the laser output is frequency-doubled to 530 nm, the species *irradiated* is the planar isomer and an initial increase in absorbance followed by a decay is now seen in the CT region (Figure 1c), while at a monitoring wavelength of 475 nm, rapid depletion of the (planar) ground state and subsequent restoration of equilibrium are observed (Figure 1d). Within experimental error, the relaxation times determined from traces such as Figure 1c were the same (0.95 ± 0.05 μsec at 24°) as the values reported above for the experiments using 1060-nm radiation.

All of the data are consistent with the interpretation that the equilibrium between the planar and tetrahedral species in their ground electronic states is perturbed by a photochemically induced concentration jump in either direction. Consequently, the exponential changes in absorbance mark the chemical relaxation of the isomerization equilibrium. In accord with this interpretation, the relaxation times were independent of concentration over the range (0.7–1.4 $\times$ 10^{-3} mol dm^{-3}) it was feasible to investigate. The kinetic data derived from the relaxation traces are considered briefly below.

We first examine some photochemical aspects of the results. The effects of irradiating the planar isomer at 530 nm are of especial interest, in view of earlier proposals by Ballhausen et al.[8] concerning the equilibrium geometry of one of the excited states of $Ni(CN)_4^{2-}$. It was suggested that excitation of an electron into the antibonding d_{xy} orbital in $Ni(CN)_4^{2-}$ destabilizes the planar structure with respect to a distorted tetrahedral structure. The present results can be accommodated by such a proposal since in planar Ni(dpp)Cl_2 the transition responsible for absorption of the laser radiation at 530 nm corresponds to the excitation of an electron into a d_{xy} orbital (using the coordinate system of ref 8) and the product which is formed within the duration of the laser pulse is the tetrahedral isomer. Furthermore, when the complex Ni(dpe)Cl_2 (exclusively planar in its ground state[4]) is irradiated at 530 nm, a rapid increase and subsequent decay in absorbance is seen in the CT region, strongly suggesting the formation of a transient tetrahedral species. The results of irradiating the tetrahedral isomer at 1060 nm point to the formation of an excited state which is distorted toward a planar structure, although the quantum yield for the formation of planar Ni(dpp)Cl_2 is low (10^{-2}). Without information on excited-state lifetimes, the significance of this low value is unclear. Overall, however, the results at both irradiation wavelengths support the view that the thermally equilibrated excited states of complexes may be distorted from their ground states.[2]

The most extensive kinetic measurements were made in acetonitrile. From the relaxation times and spectrophotometrically determined equilibrium constant[9] $K = k_s/k_t$, both measured over the temperature range 10–50°, the following kinetic and thermodynamic parameters were obtained

$$\underset{\text{(planar)}}{\mathrm{Ni(dpp)Cl_2}} \underset{k_t}{\overset{k_s}{\rightleftharpoons}} \underset{\text{(tetrahedral)}}{\mathrm{Ni(dpp)Cl_2}}$$

$$K^{23°} = k_s/k_t = 0.75;\ \Delta H° = 7 \pm 1\ \mathrm{kJ\ mol^{-1}};$$

$$\Delta S° = 20 \pm 2\ \mathrm{J\ K^{-1}\ mol^{-1}}\quad k_s^{23°} = 4.5 \times 10^5\ \mathrm{sec^{-1}},$$

$$k_t^{23°} = 6 \times 10^5\ \mathrm{sec^{-1}}$$

Activation parameters, determined from a plot of log k/T against T^{-1}, were $\Delta H_t^{\ddagger} = 35 \pm 1$ kJ mol^{-1}; $\Delta S_t^{\ddagger} = -15 \pm 4$ J K^{-1} mol^{-1}. These rate constants are of the same order as have been reported[1] for related complexes investigated by NMR but much slower than for bischelate complexes.[1a] These systems, where $k_t^{298} > 10^7$ sec^{-1} is expected, are outside the range of NMR but are likely to be within the scope of the present method where the principal limitation is the laser pulse duration.

Finally we note that a useful link is beginning to emerge between the reactivity of the photoexcited states of transition metal complexes and structural equilibria involving such complexes in their ground electronic states. Specific photodissociation[10] or electron transfer[11] processes or, as in the present case, an excited state distortion may provide convenient means of perturbing such equilibria and hence, through chemical relaxation,[12] of studying the kinetics of interconversions.

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References and Notes

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(5) The effective symmetry is C_{2v} but the spectra can be interpreted in terms of the point group T_d. See ref 6.

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(9) Measured at 475 nm, assuming ϵ_{475} 1510 M^{-1} cm^{-1} for the planar isomer; this value of ϵ_{475} is that measured in acetonitrile for the complex Ni(dpe)Cl$_2$ which exists exclusively (ref 4) in the planar form. Dpe is 1,2-bis(diphenylphosphino)ethane.

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Antiport Regulation of Carrier Mediated Chiroselective Transport through a Liquid Membrane[1]

Sir:

Selective transport of amino acids through a liquid membrane by lipophilic carrier molecules has been described.[2] Coupling to acid–base reactions and to cation gradients was used to pump the transport process. pH effects on trans-membrane diffusion of weak acids has also been observed in biological model systems (see for instance ref 3 and references therein).

We wish to report regulatory effects of the counter transported (antiport) species on *chiroselective transport* by a chiral carrier molecule, i.e., on preferential transport of one optical antipode of a racemic substrate. The carrier was the optically active hydrochloride of (−)-*N*-(1-naphthyl)methyl α-methylbenzylamine[4,5] ((−)T$^+$Cl$^-$, $\mathrm{C_6H_5CH(CH_3)N^+H_2CH_2\text{-}\alpha\text{-}C_{10}H_7}$, Cl$^-$; [α]D = −22.2 ± 0.4°, *c* 3.565, CHCl$_3$) dissolved in chloroform, and the substrate was racemic sodium mandelate, S$^-$Na$^+$, in water.[6] This system displays partial resolution by extraction of S$^-$ by T$^+$ from water into chloroform.[4] The experiments were performed in a setup consisting of a stirred chloroform membrane M separating two stirred water phases IN and OUT,[2,7] which contained initially (±) sodium mandelate and the sodium salts of different acids, A$^-$Na$^+$, respectively. The amount and optical rotation of mandelate in all three phases was followed as a function of time.

(1) When the carrier T$^+$ is added to the membrane, mandelate S$^-$ and the antiport anion A$^-$ are taken up and exchanged across the interfaces, so that S$^-$ and A$^-$ appear simultaneously in the OUT and IN phases, respectively. In the absence of carrier in M the leakage of mandelate (or mandelic acid) through the membrane is negligible (<2 μmol/(hr cm^2)). Since both antipodes of mandelate are competing for the carrier, the transport process may be described as *competition flux* of (+)S$^-$ and (−)S$^-$ in *exchange diffusion* with A$^-$ (see for instance ref 8) mediated by the carrier T$^+$. It may present both flux stimulation, as is generally possible in exchange diffusion,[8] and substrate selectivity via the diastereomeric pairs [(−)T$^+$, (+)S$^-$] and [(−)T$^+$, (−)S$^-$] formed in M. Table I and Figure 1 give results for a variety of antiport anions.

(2) Sodium mandelate, initially racemic in IN, becomes optically active in all three phases. Thus, the transport process is *chiroselective.* Although the maximum optical resolution obtained (<10%) is at most equal to that of a two-

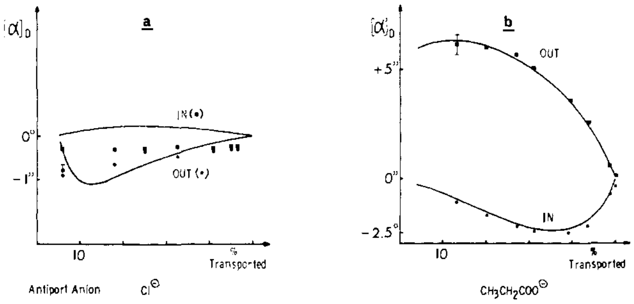

Figure 1. Variation of the specific optical rotation [α]D of mandelate in the IN and OUT phases as a function of per cent mandelate transported when the antiport anion is chloride (a) or propionate (b) (see also footnote to Table I). The points are experimental results and the curves are computed as described in ref 11. Because resolution of the transport equations[11] would have been much more involved, the amount of mandelate extracted from IN into M was neglected. The calculated curves should be displaced toward the bottom of the figures (to about [α]D = −0.3° for IN, Cl$^-$ case) leading to agreement with the experimental numbers.