Contribution from the Department of Chemistry,
The Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland

Laser Photochemical Perturbation and Relaxation Kinetics of Rapid Planar ⇌ Square-Pyramidal Interconversions in Complexes of Nickel(II) with Open-Chain and Macrocyclic Ligands

LOUIS CAMPBELL, JOHN J. McGARVEY,* and NICOLAS G. SAMMAN

Received April 4, 1978

Nanosecond laser flash photolysis in aqueous solution of the paramagnetic five-coordinate complex $NiL(H_2O)$, where L is the open-chain quadridentate ligand 1,5-diazacyclooctane-*N,N′*-diacetate (dacoda), results in the rapid formation of the diamagnetic, planar species NiL. Similar irradiation experiments in aqueous solutions of the nickel(II) complex with the macrocyclic ligand 2,4,4-trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene (AEX) gave analogous results, reflecting a five-coordinate ⇌ four-coordinate equilibrium, $Ni(AEX)(H_2O)^{2+} \rightleftharpoons Ni(AEX)^{2+} + H_2O$. For both complexes, the transient absorbance changes are explained in terms of the ligand field transitions responsible for absorption of the 1060-nm laser radiation, $^3A_2 \leftarrow {}^3B_1$ (dacoda complex) and $^3E \leftarrow {}^3B_1$ (AEX complex), leading to the population of a_1 (d_{z^2}) orbitals with consequent weakening of metal–apical ligand bonds. The two systems constitute novel examples of the link between coordinative distortion and the spin states of some five-coordinate complexes. The rate constants at 20 °C for the first-order singlet → triplet conversions computed from the absorbance relaxation traces are $k_{s\to t}(\text{dacoda}) \geq 4 \times 10^7$ s^{-1} and $k_{s\to t}(\text{AEX}) = 4.5 \times 10^6$ s^{-1}. A possible explanation for the tenfold difference in k is considered.

Introduction

It was pointed out some years ago[1] that the reactivity of transition-metal complexes with respect to isomerization and ligand substitution could be enhanced by the angular redistribution of electron density following irradiation in their ligand field bands. Recent investigations in this laboratory[2-4] using Q-switched laser techniques have shown that ligand field photochemistry in transition-metal complexes can afford a convenient route to the study of the fast chemical relaxation kinetics of perturbed ground-state equilibria in such systems. This previous work has been concerned with bond dissociation in octahedral and five-coordinate complexes and with planar ⇌ tetrahedral isomerizations. Recently, an instance has been reported[5] where the perturbation of equilibrium is preceded by a photoassociation reaction, the occurrence of which was linked to an excited-state distortion resulting from changes in d-orbital populations.

The possibility of effecting rapid changes in the population of antibonding orbitals and hence changes in spin state is of particular interest in the case of five-coordinate complexes of nickel(II) in which, as pointed out in a recent review,[6] there is a correlation between spin state and coordinative distortion. Thus, low-spin, square-pyramidal complexes of Ni(II) often have a long metal–apical ligand bond and a d-orbital splitting pattern akin to that of a square-planar complex. Since previous work has clearly demonstrated that laser photochemical excitation provides a way of effecting a change in the population of antibonding orbitals and hence of spin state, a route to the kinetics of fast four-coordinate ⇌ five-coordinate (diamagnetic ⇌ paramagnetic) interconversions may be available in some circumstances. We report here our observations on two complexes which bear out these expectations.

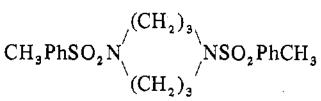
In one of the two complexes, high-spin, five-coordinate $Ni(dacoda)(H_2O)$ (dacoda is the open-chain quadridentate ligand 1,5-diazacyclooctane-*N,N′*-diacetate), first reported by Legg et al.,[7] electronic spectra strongly suggest that the square-pyramidal (high-spin) geometry established[8] for the solid is retained in aqueous solutions.[9] The other complex, $Ni(AEX)^{2+}$ (AEX is the macrocyclic ligand 2,4,4-trimethyl-10,11-benzo-1,5-diaza-8,13-dithiacyclopentadeca-1,10-diene), diamagnetic and square planar in the solid, showed in aqueous solution additional weak absorption in the spectral region corresponding to high-spin, five-coordinate nickel(II). These features led Urbach and Busch[10] to propose a square-planar ⇌ five-coordinate equilibrium, $Ni(AEX)^{2+} + H_2O \rightleftharpoons Ni(AEX)(H_2O)^{2+}$. No further evidence was put forward at that time in favor of this proposal. It seemed likely that $Ni(AEX)(H_2O)^{2+}$ would have a square-pyramidal geometry like that of $Ni(dacoda)(H_2O)$, and a study of the Q-switched laser irradiation of both complexes appeared worthwhile, bearing in mind the link mentioned earlier between spin state and geometric distortion.

Experimental Section

$Ni(AEX)Cl_2(H_2O)$. This complex was prepared by the method of Urbach and Busch[10] and recrystallized from methanol.

$Ni(dacoda)(H_2O)$. The complex was prepared according to the method reported by Legg et al.[9] but with the following modified procedure for preparation of the ligand 1,5-diazacyclooctane (daco) from which the dacoda complex was then made.

Fifty grams of the sulfonamide



$$CH_3PhSO_2N\underset{(CH_2)_3}{\overset{(CH_2)_3}{\Big\langle\quad\Big\rangle}}NSO_2PhCH_3$$

in a mixture of 360 mL of glacial acetic acid and 240 mL of 48% hydrobromic acid was heated under reflux for ca. 8 h. The cooled mixture was filtered and the filtrate reduced to a small volume. After the filtrate was cooled, a solid formed which was digested in 50 mL of ethanol, yielding a crop of white needles of 1,5-diazacyclooctane dihydrobromide, mp (after recrystallization) 258–260 °C.

Anal. Calcd for $C_6H_{16}Br_2N_2$: C, 26.11; H, 5.84; N, 10.15; Br, 57.90. Found: C, 26.14; H, 5.83; N, 10.32; Br, 57.68. Aqueous solutions of the complex were irradiated at 1060 nm with a Q-switched neodymium laser, half-peak pulse width 30 ns, with incident pulse energies in the range 300–500 mJ. The spectrophotometric monitoring system (response time ~20 ns) consisted of a 150-W xenon arc with a current-boosted output (1-ms boost duration) to enhance signal-to-noise ratios, a Bausch and Lomb high-intensity monochromator, and a 1P28 photomultiplier with a five-dynode stage circuit of the type first described by Hunt and Thomas.[11] Transient absorbance changes were recorded on a Tektronix 7904 oscilloscope.

Results and Discussion

(a) Photochemical Aspects. $Ni(AEX)Cl_2(H_2O)$. When aqueous solutions of the complex were irradiated at 1060 nm, there was a rapid increase (within the laser pulse) in absorbance in the wavelength range 420–540 nm followed by a return to almost the original absorbance level. Figure 1A shows a sample trace. The time constant of this relaxation process varied with temperature but was independent of complex concentration ((0.75–2.5) × 10^{-2} mol dm^{-3}). The relevant data are in Table I. The differential absorbance spectrum derived from the transient traces is plotted in Figure 2. Also shown is the temperature difference spectrum of

0020-1669/78/1317-3378$01.00/0

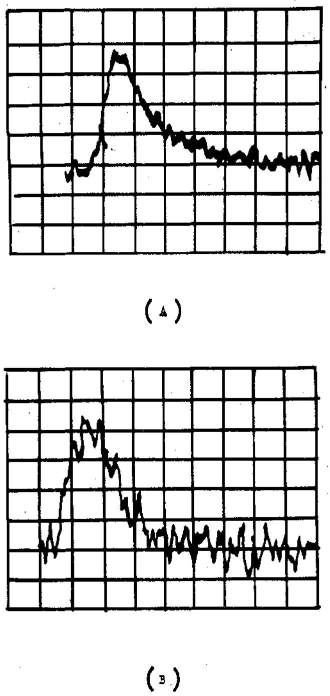


Figure 1. Absorbance changes, of aqueous solutions of complex at 7 °C as a function of time following laser irradiation at 1060 nm: (A) $Ni(AEX)(H_2O)^{2+}$ (10^{-2} mol dm^{-3}; λ_{mon} 475 nm, initial absorbance ~0.3; vertical scale, 0.25% absorbance change/division; time base, 50 ns/division); (B) $Ni(dacoda)(H_2O)$ (0.25 mol dm^{-3}; λ_{mon} 480 nm, initial absorbance ~0.7; vertical scale, 0.3% absorbance change/division; time base, 20 ns/division).

Table I. Influence of Temperature and Concentration on the Relaxation Time[a] of the Photochemically Perturbed Equilibrium $Ni(AEX)(H_2O)^{2+} \rightleftharpoons Ni(AEX)^{2+} + H_2O$

$10^{-3}C$, mol dm^{-3}	10	10	7.5	25
temp, °C	7	20	20	20
τ, ns	69 ± 7	50 ± 3	43 ± 5	43 ± 3

[a] Errors are estimates based upon analysis of at least four relaxation traces.

$Ni(AEX)Cl_2(H_2O)$ in aqueous solution, derived from absorption spectra of the complex recorded on a conventional spectrophotometer (Perkin-Elmer Model 402) at 20 and 50 °C. This Δt spectrum is clearly consistent with the original proposal[10] of an equilibrium between diamagnetic, planar $Ni(AEX)^{2+}$ and paramagnetic, five-coordinate $Ni(AEX)(H_2O)^{2+}$. The close agreement between the Δt and the ΔA spectra in the wavelength range (420–550) nm indicates that it is this same equilibrium which is photochemically perturbed by the laser pulse. This is readily understandable if it is assumed that the absorbing species at the laser wavelength is five-coordinate $Ni(AEX)(H_2O)^{2+}$. It is reasonable to assume an essentially square-pyramidal structure for this complex, with the water ligand occupying the apical position. If we take the *effective* symmetry as C_{4v}, the transition responsible for absorption of the laser radiation at 1060 nm may be assigned[10] $^3E \leftarrow {}^3B_1$, corresponding to the promotion of an electron from the e (d_{xz}, d_{yz}) orbitals to the d_{z^2} orbital, leaving the latter orbital doubly occupied. As a result, we may expect the axial bond strength to be drastically reduced.[12] The resultant stabilization of the d_{z^2} orbital leaves a d-orbital splitting pattern which approximates to that of a square-planar field.[13] The photochemical displacement toward the planar species, of the equilibrium between $Ni(AEX)(H_2O)^{2+}$ and $Ni(AEX)^{2+}$, is thus satisfactorily accounted for. The small temperature rise in the system marked by the decay of absorbance to a level slightly higher[14a] than before the laser pulse provides further support for the existence of an equilibrium of this type. The direction of the displacement is consistent with the endothermicity of the five-coordinate → planar process as shown by the Δt spectrum in Figure 2. As in the case of the analogous effect observed[2] following the Q-switched laser irradiation of the polyamine complex $Ni(2,3,2\text{-tet})(H_2O)_2^{2+}$, the temperature rise may be reasonably attributed[14b] to a nonradiative decay of excited $Ni(AEX)(H_2O)^{2+}$.

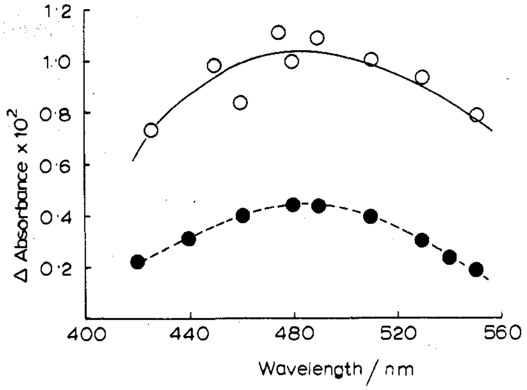


Figure 2. Temperature difference spectrum (filled circles) of aqueous $Ni(AEX)Cl_2(H_2O)$ (10^{-2} mol dm^{-3}) and absorbance difference spectrum (open circles) of same solution following laser photolysis at 1060 nm. Ordinate for Δt spectrum is 100 times indicated scale.

The other feature of the behavior of the AEX system which requires comment is the gradual disappearance over a period of a few hours at 20 °C of the photochemical activity of $Ni(AEX)Cl_2(H_2O)$ solutions. It has been noted by Urbach and Busch[10] that the $Ni(AEX)^{2+}$ complex is hydrolytically unstable and decomposes in aqueous solution to give the octahedral species[15] $Ni(EX)(H_2O)_2^{2+}$. This appears to be the explanation of the gradual onset of photoinertness in the $Ni(AEX)Cl_2(H_2O)$ solutions. Aqueous solutions of $Ni(EX)Cl_2(H_2O)$, which showed typical high-spin spectra due to the species $Ni(EX)(H_2O)_2^{2+}$, did indeed prove to be photoinactive when irradiated at 1060 nm. This is surprising, in view of the established photochemical activity[2,16] of a range of complexes of the type $NiL(H_2O)_2^{2+}$, where L is a quadridentate polyamine ligand. The explanation may lie with the occurrence of very efficient deactivation pathways of the initially populated excited state such as have been observed recently in investigations of metal complexes by picosecond laser techniques.[17]

Ni(dacoda)(H₂O). Figure 1B illustrates the very rapid increase in absorbance at 490 nm and the subsequent decay when an aqueous solution of $Ni(dacoda)(H_2O)$ was irradiated at 1060 nm. The effect is very similar to that observed with $Ni(AEX)(H_2O)^{2+}$ but the decay is considerably faster. The average relaxation time determined from more than 20 traces is $\tau = 25 \pm 5$ ns. There was no observable variation of τ with either temperature or concentration of complex.[18] Similar traces were recorded throughout the wavelength range (460–530) nm. The derived absorption spectrum is shown in Figure 3. For comparison, the figure shows the reflectance spectrum of solid planar Ni(dacoda), prepared by heating the green five-coordinate $Ni(dacoda)(H_2O)$.[9] The agreement between these spectra is sufficient to conclude that the species produced by the laser pulse is either planar Ni(dacoda) or perhaps $Ni(dacoda)(H_2O)$ in which the apical $Ni\text{–}OH_2$ bond has been lengthened considerably. As in the case of $Ni(AEX)(H_2O)^{2+}$, the photochemical formation of a planar species can be accounted for by considering the assignment of the spectral transition at 1060 nm. In the case of $Ni(dacoda)(H_2O)$, for C_{4v} symmetry, the transition has been assigned[9] as $^3A_2(e^4b_2^1a_1^2b_1^1) \leftarrow {}^3B_1(e^4b_2^2a_1^1b_1^1)$. Again as for the AEX complex, the doubly occupied a_1 (d_{z^2}) orbital in the

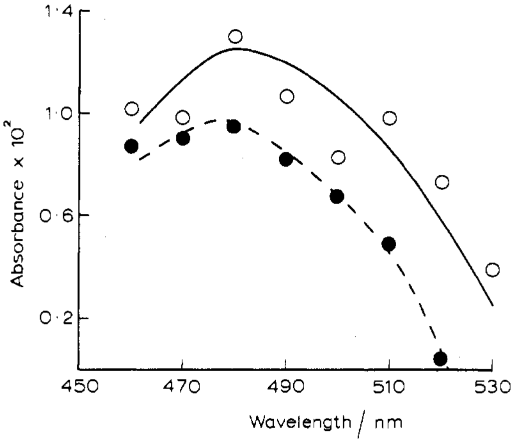


Figure 3. Electronic reflectance spectrum (filled circles) of solid, planar Ni(dacoda) and absorption spectrum (open circles) of transient formed in laser photolysis at 1060 nm of Ni(dacoda)(H_2O) (0.25 mol dm^{-3}). Ordinate for reflectance spectrum is in arbitrary units.

excited $^3A_2$ state is expected to lead to a lengthening of the apical Ni–OH_2 bond. The link between certain types of geometric distortion and the spin state of five-coordinate complexes of Ni(II) has been referred to already. In particular, lengthening the apical bond in complexes of square-pyramidal geometry tends to stabilize the low-spin state. In the examples reported here, the necessary bond lengthening is effected photochemically and the transient spectra recorded do indeed suggest that, in both instances, the species produced in the laser pulse are planar.

(b) Kinetic Aspects. The photochemically perturbed equilibria are both accompanied by a spin change of $\Delta S = 1$. The kinetics of rapidly established spin equilibria of this type have become of increasing interest in the last few years with the advent of sufficiently fast chemical relaxation techniques. It is thus useful to consider the kinetic data for the $Ni(AEX)^{2+}$ and Ni(dacoda)(H_2O) complexes alongside data for other spin-state systems.[19]

$\mathrm{Ni(AEX)(H_2O)} \underset{k_f}{\overset{k_b}{\rightleftharpoons}} \mathrm{Ni(AEX)^{2+} + H_2O}$. In the pseudo-first-order kinetic conditions which prevail in aqueous solution, the forward and reverse rate constants k_f and k_b can be obtained in the usual fashion from the expressions for τ^{-1} and K, $\tau^{-1} = k_f + k_b$ and $K = k_f/k_b$, provided K is available. A value of 30 mol^{-1} cm^{-1} for ϵ_{490} of the species $Ni(AEX)^{2+}$, from the data of Urbach and Busch,[10] together with our own absorbance measurements at 20 °C used in the determination of the Δt spectrum shown in Figure 2, gave $K = 0.3$ and the forward and reverse rate constants at 20 °C, $k_f = 4.5 \times 10^6$ s^{-1} and $k_b = 1.5 \times 10^7$ s^{-1}. These values are in the range observed for a number of spin-state interconversions in Fe(II), Fe(III), and Co(II) complexes for which it has been suggested that nonelectronic factors may be rate determining.[19] The results of the present work are consistent with this view since the singlet $\rightleftharpoons$ triplet spin change is accompanied by fairly substantial coordination sphere reorganization. In the case of Ni(dacoda)(H_2O), taking $\tau = 25$ ns at 20 °C, gives as a lower limit[18] for the rate constant of the singlet to triplet conversion 4×10^7 s^{-1}, a factor of 10 faster than that for the $Ni(AEX)^{2+}$ process. This difference may be associated with the hydrophobic character of the macrocyclic AEX ligand which, it has been suggested,[10] may structure the surrounding water to an extent that coordination to the complex ion becomes difficult. It will be of interest in future investigations to try to establish the relative contributions of enthalpic and entropic barriers to the magnitude of the singlet → triplet rate constant in the $Ni(AEX)^{2+}$ system.

In conclusion, the experiments reported here, taking advantage of the connection between spin state and coordinative distortion in metal complexes, are a further illustration of the usefulness of the laser photochemical method as a means of investigating the chemical relaxation of perturbed equilibria with the participating species in their ground electronic states. For systems where the photophysical behavior of the initially populated excited states is favorable, the method may prove superior to the widely employed temperature-jump technique where an unfavorable position of equilibrium or a small enthalpy change may preclude or impair its application.

Acknowledgment. We thank the Science Research Council for a postdoctoral fellowship (to N.S.) and a grant in support of some of this work and also the Department of Education (Northern Ireland) for a postgraduate studentship (to L.C.).

Registry No. $Ni(AEX)(H_2O)^{2+}$, 67761-31-3; Ni(dacoda)(H_2O), 56604-45-6; daco-*N,N'*-Ts_2, 67761-04-0; daco·2HBr, 40422-46-6.

References and Notes

(1) V. Balzani, L. Moggi, and V. Carassiti, *Ber. Bunsenges. Phys. Chem.*, **72**, 288 (1968).
(2) K. J. Ivin, R. Jamison, and J. J. McGarvey, *J. Am. Chem. Soc.*, **94**, 1763 (1972).
(3) H. Hirohara, K. J. Ivin, J. J. McGarvey, and J. Wilson, *J. Am. Chem. Soc.*, **96**, 4435 (1974).
(4) J. J. McGarvey and J. Wilson, *J. Am. Chem. Soc.*, **97**, 2531 (1975); L. Campbell and J. J. McGarvey, *J. Chem. Soc., Chem. Commun.*, 749 (1976).
(5) L. Campbell and J. J. McGarvey, *J. Am. Chem. Soc.*, **99**, 5809 (1977).
(6) R. Morassi, I. Bertini, and L. Sacconi, *Coord. Chem. Rev.*, **11**, 343 (1973).
(7) J. I. Legg, D. O. Nielson, D. L. Smith, and M. L. Larson, *J. Am. Chem. Soc.*, **90**, 5030 (1968).
(8) D. O. Nielson, M. L. Larson, R. D. Willett, and J. I. Legg, *J. Am. Chem. Soc.*, **93**, 5079 (1971).
(9) D. F. Averill, J. I. Legg, and D. L. Smith, *Inorg. Chem.*, **11**, 2344 (1972).
(10) F. L. Urbach and D. H. Busch, *Inorg. Chem.*, **12**, 408 (1973).
(11) J. W. Hunt and J. K. Thomas, *Radiat. Res.*, **32**, 149 (1967).
(12) J. K. Burdett, *Inorg. Chem.*, **15**, 212 (1976).
(13) P. L. Orioli and C. A. Ghilardi, *J. Chem. Soc. A*, 1511 (1970).
(14) (a) This effect was quite reproducible and traces recorded at longer sweep times showed that the decay to a higher absorbance was genuine and not simply due to experimental scatter. (b) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **95**, 7177 (1973).
(15) EX is the ligand 1,10-diamino-3,8-dithia-5,6-benzodecene.
(16) L. Campbell, J. J. McGarvey, and J. Wilson, to be submitted for publication. As well as the 2,3,2-tet and trien complexes of Ni(II),[2] the complexes of the 3,2,3-tet and 3,3,3-tet homologues have also been found to be photoactive.
(17) A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley, and M. W. Windsor, *Chem. Phys. Lett.*, **37**, 199 (1976).
(18) The laser pulse duration is a limiting factor here. Some improvement in the estimate for τ could probably be obtained by a deconvolution procedure, such as described recently by E. V. Dose, M. F. Tweedle, L. J. Wilson, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 3886 (1977).
(19) E.g., M. G. Simmons and L. J. Wilson, *Inorg. Chem.*, **16**, 126 (1977), and references therein.