with tetraarylporphines[16,17] indicate the extreme flexibility of the porphyrin nucleus. We assume that the incoming protons attack the opposite pyrrole nitrogens, two protons for ZnP and one for Zn-*N*-MeP. This causes the porphyrin to bend, moving the opposite pyrrole planes downward and the other two upward, thus lifting the now two-coordinate zinc ion above and away from the porphyrin. The initial two- and one-proton attacks formally form the neutral free-base species of ZnP and Zn-*N*-MeP, balancing in a concerted fashion the incipient di- and uninegative porphyrin charges caused by the gradual removal of zinc. Halide ions could plausibly occupy the coordination positions vacated by the protonated nitrogen atoms, further reducing the amount of charge separation needed for dissociation. The rate increase with porphyrin basicity is reasonable in terms of proton attack at the nitrogen positions. The final step for both porphyrin types is a one-proton attack on either of the two remaining nitrogen atoms bonded to zinc, with the resulting one-coordinate zinc ion being readily displaced. The idea of successive porphyrin protonations and metal ion ligations (by H_2O and pyridine with[5] MgP) which balance charge, deform the porphyrin, and reduce the coordination number of the porphyrin to the metal ion is a possible model for solvolysis reactions of such rigid macrocyclic complexes.

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[16] L. K. Gottwald and E. F. Ullman, *Tetrahedron Lett.*, 3071 (1969).

[17] P. Hambright, *Coord. Chem. Rev.*, in press.

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Temperature Dependence of the Ligand-Field Spectra of Some Five-Coordinate Complexes Containing Nickel(II), Palladium(II), and Platinum(II)[1]

Sir:

A substantial amount of electronic spectral data is now available for low-spin trigonal-bipyramidal complexes containing nickel(II),[2] palladium(II),[3] and platinum(II).[3] In a D_{3h} environment the two lowest energy bands ν_1 and ν_2 should correspond to the ${}^1A_1' \rightarrow {}^1E'$ and ${}^1A_1' \rightarrow {}^1E''$ transitions, respectively,[4,5] with the latter being orbitally forbidden. If the metal is in a C_{3v} environment both the ${}^1A_1 \rightarrow a{}^1E$ and ${}^1A_1 \rightarrow b{}^1E$ transitions are allowed, although the latter still has low intensity.[2] The lowest frequency band ν_1 is usually asymmetric,[6] and even may be split into a double peak[5,7] at room temperature. At this temperature the splitting of ν_1 has been interpreted as a result of a small ground-state distortion which removes the degeneracy of the ${}^1E'$ (or $a{}^1E$) state.[3-7]

We have carried out electronic spectral measurements at temperatures down to 77°K (or in some cases to 100°K) on solutions of complexes of the type $[Ni(CN)_2(PhPR_2)_3]$ (R = Me, OEt) and $[MX(L'L_3)]^+$, where M = Ni(II), Pd(II), Pt(II), X = a unidentate anion, and $L'L_3$ represents the quadridentate "tripod-like" ligands $(Me_2AsCH_2CH_2CH_2)_3L'$ (L' = P, TAP; L' = As, TAA), $(o\text{-}MeL \cdot C_6H_4)_3P$ (L = S, TSP; L = Se, TSeP), and $(o\text{-}Ph_2L \cdot C_6H_4)_3L'$ (L' = L = P, QP; L' = L = As, QAS). In all cases, on cooling, the asymmetric or split band ν_1 exhibits a dramatic increase in extinction coefficient and becomes more symmetrical.

The ligand-field spectrum of $[Ni(CN)_2\{PhP(OEt)_2\}_3]$ in 2-methyltetrahydrofuran–ethanol (2:1 by volume) is shown in Figure 1. The two bands (at 24,000 and 27,500 cm^{-1}) contributing to the ${}^1A_1' \rightarrow {}^1E'$ transition ν_1 at 295°K are found to merge as the temperature is decreased and a single symmetrical band is obtained at 77°K. The low-energy region of the electronic spectrum of [PtCl(QP)]Cl in 2-methyltetrahydrofuran–dichloromethane (9:1) is given in Figure 2; again ν_1 becomes more symmetrical as the temperature is lowered, but even at 100°K the ${}^1A_1 \rightarrow a{}^1E$ bandenvelope retains some asymmetry. The oscillator strength of ν_1 remains approximately independent of temperature for both compounds, as expected for a symmetry-allowed band.

The tendency of ν_1 to become more symmetrical at low temperatures is extremely unusual spectroscopic behavior and suggests that in solution there is either (1) a temperature-dependent static distortion of the ground state or (2) a Jahn–Teller distortion of the doubly degenerate excited state.

The energy difference between the idealized trigonal-bipyramidal and square-pyramidal structures of five-coordinate molecules, especially those containing monodentate ligands, is usually small.[8] As the potential energy surface connecting these two forms is irregular,[8] molecules of intermediate structure might be favored under certain solvent and temperature conditions.[9] The temperature variation of ν_1 using interpretation 1 could be analyzed in terms of an equilibrium between the two forms: regular trigonal bipyramid (D_{3h} or C_{3v}) $\rightleftharpoons$ distorted trigonal bipyramid(C_{2v} or C_s).

At temperatures between 295 and 77°K (or 100°K) an equilibrium mixture would be obtained, and three bands in the region of ν_1 would be predicted. In no case, however, have more than two bands been observed. A more satisfactory explanation of the temperature dependence of ν_1 using the ground-state distortion model is to consider that species of intermediate geometry are present at intermediate tem-

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[1] Part of this research was supported by the National Science Foundation.

[2] For recent reviews, see C. Furlani, *Coord. Chem. Rev.*, 3, 141 (1968); L. Sacconi, *Pure Appl. Chem.*, 17, 95 (1968); M. Ciampolini, *Struct. Bonding (Berlin)*, 6, 52 (1969).

[3] G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 2771 (1965), and references therein.

[4] M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *ibid.*, *A*, 540 (1967); *Coord. Chem. Rev.*, 2, 99 (1967).

[5] B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 3994 (1968).

[6] G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, 3, 1544 (1964); G. S. Benner and D. W. Meek, *ibid.*, 6, 1399 (1967); L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 90, 5443 (1968).

[7] B. B. Chastain, D. W. Meek, E. Billig, J. E. Hix, Jr., and H. B. Gray, *Inorg. Chem.*, 7, 2412 (1968); J. W. Dawson, D.Phil. Thesis, Oxford University, 1970.

[8] E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

[9] In the *solid* state, complexes $[Ni(CN)_2(PhPR_2)_3]$ (R = OEt, Me) are significantly distorted from trigonal-bipyramidal toward square-pyramidal geometry; see J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1084, 1090 (1969).

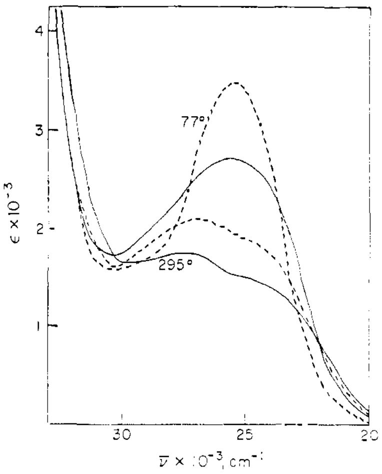

Figure 1. Ligand-field spectrum of $[Ni(CN)_2\{PhP(OEt)_2\}_3]$ as a function of temperature (°K).

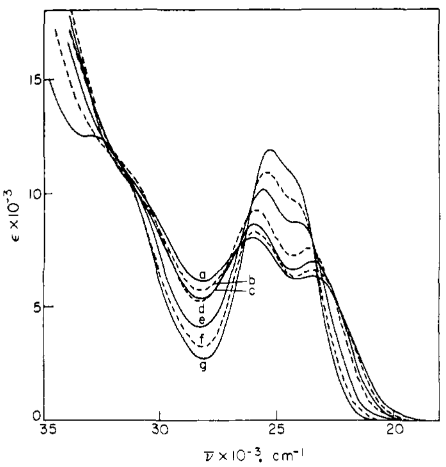

Figure 2. Ligand-field spectrum of [PtCl(QP)]Cl as a function of temperature (°K): a, 295°; b, 258°; c, 207°; d, 156°; e, 132°; f, 119°; g, 100°.

peratures, the actual structure depending on the magnitude of, *e.g.*, solute–solvent interactions at a given temperature. The appearance of ν_1 would then reflect the amount of distortion in this intermediate structure.

The dynamic Jahn–Teller effect could also account for both the splitting of the low-energy band ν_1 and its temperature dependence, provided that the trigonal-bipyramidal complexes have a regular or nearly regular structure in *solution.* Those vibrations which are Jahn–Teller active must have nonvanishing matrix elements of the form $\langle k|\partial\mathcal{H}/\partial Q_i)_0|k\rangle$, where $\mathcal{H}$ is the total Hamiltonian of the system, Q_i is a nuclear displacement, and k represents an electronic state.[10] If $(\partial\mathcal{H}/\partial Q_i)_0$ and $|k\rangle$ transform as components of the irreducible representations Γ' and Γ, respectively, then for matrix elements to be nonzero, Γ' must be contained in the symmetric direct product $[\Gamma]^2$. It is found that in D_{3h} symmetry the three ϵ' vibrations can lift the degeneracy of both E′ and E″ excited electronic states, and that in C_{3v} symmetry the four ϵ vibrations will split the E levels. A system involving interaction of an E electronic level with several doubly degenerate vibrational modes[11] behaves similarly to one involving a single pair of ϵ modes, and the separation $\Delta\nu_1$ of the two components of transition ν_1 is obtained by summing[10,12] over all Jahn–Teller-active $\epsilon(')$ vibrations to give

$$(\Delta\nu_1)^2 = \sum_{i=1}^{n}(2A_i^2\hbar/\mu_i\omega_{\epsilon i}) \coth(\hbar\omega_{\epsilon i}/2kT)$$

where $2A$ is the splitting of an E electronic term by unit distortion, μ is the reduced mass of the vibrating atoms, ω_ϵ is the frequency of an $\epsilon(')$ normal mode, and T is the temperature. Thus a decrease in $\Delta\nu_1$ with decreasing temperature is predicted, as is found here.

Finally, it should be noted that preliminary experiments on the solid complexes (in the form of thin films on silica plates) show that there is hardly any change in $\Delta\nu_1$ on lowering the temperature, in marked contrast to the behavior in solution. It appears that in the *solid* state the asymmetry or splitting of ν_1 is due primarily to a ground-state distortion. Full results and a more extensive discussion of the relative merits of the variable ground-state distortion and dynamic Jahn–Teller approaches will be published later.

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[10] M. D. Sturge, *Solid State Phys.*, **20**, 91 (1967).

[11] J. C. Slonczewski, *Phys. Rev.*, **131**, 1596 (1963).

[12] M. C. M. O'Brien, *Proc. Phys. Soc., London*, **86**, 847 (1965).

Secondary Deuterium Isotope Effects on Triplet Excitation Transfer. Deuterium Position and Sensitizer Effects

Sir:

Secondary deuterium isotope effects have been found useful in understanding bimolecular photochemical interactions.[1-3] We have previously examined isotope effects in an excitation-transfer system, the photosensitized trans–cis isomerization of β-methylstyrene.[1] We now report extension of those studies to include other sensitizers and other positions of label in β-methylstyrene. The following principal conclusions result: (1) the isotope effect on partitioning of the olefin triplet to cis and trans ground states is nil; (2) significant involvement of remote positions in the excitation-transfer process occurs; (3) sensitizers with widely differing types of chromophore show essentially identical isotope effects, emphasizing the similarity of the bimolecular interactions; and (4) the origins of the deuterium isotope effect are probably more closely allied with the effect of deuterium on excitation en-

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[1] R. A. Caldwell and G. W. Sovocool, *J. Amer. Chem. Soc.*, **90**, 7138 (1968).

[2] M. W. Schmidt and E. K. C. Lee, *ibid.*, **90**, 5919 (1968).

[3] (a) R. A. Caldwell and S. P. James, *ibid.*, **91**, 5184 (1969); (b) R. A. Caldwell, *ibid.*, **92**, 1439 (1970).