known[19] to exist in aqueous solutions in an equilibrium with $LNi(H_2O)_2^{2+}$.

$$LNi^{2+}(aq) + 2H_2O \rightleftharpoons LNi(H_2O)_2^{2+} \qquad (13)$$

The octahedral complex $LNi(H_2O)_2^{2+}$ has the high-spin electronic configuration.[19] Pressure-dependence studies of this equilibrium reaction revealed that $\Delta\bar{V}_{13}$ is considerably smaller than expected, i.e. $\Delta\bar{V}_{13} = -1.2 \pm 0.1$ cm^3 mol^{-1} [20] or $\Delta\bar{V}_{13} = -3.5 \pm 0.1$ cm^3 mol^{-1}.[21] The authors assumed that these small volumes of reaction stem from a cancellation of a negative $\Delta\bar{V}$ coordination by a positive $\Delta\bar{V}$ expansion. The latter value stems from the change from low spin to high spin and was estimated to contribute 8.1 cm^3 mol^{-1} for the nickel–cyclam complex. This process clearly cannot contribute to $\Delta V^{\ddagger}_1$. The results thus seem to suggest that two axial water molecules, though not bound to the nickel, occupy the cavities formed by the ligand. These water molecules block the approach of the $^{\bullet}CH_3$ free radical to the central cation, and one of them has to be partially extricated from the cavity prior to the nickel–carbon bond formation. This process, which is speculative at this stage, explains the small positive value of $\Delta V^{\ddagger}_1$. We plan to extend this study to similar systems in order to check this hypothesis.

Acknowledgment. We wish to thank D. Carmi, Y. Nahon, and Y. Nehemia for technical assistance. This research was supported in part by a grant from G.I.F., the German-Israeli Foundation for Scientific Research and Development, and by a grant from the Israeli Academy of Sciences and from the Planning and Granting Committee of the Council for Higher Education and the Israel Atomic Energy Commission. D.M. expresses his appreciation to Mrs. Irene Evens for her continuous interest and support.

Registry No. $(cyclam)(H_2O)Ni^{III}{-}CH_3^{2+}$, 117687-73-7.

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(17) The spin state of the complex $L(H_2O)Ni^{III}{-}CH_3^{2+}(aq)$ is not known. However, all other $L(H_2O)Ni^{III}{-}X$ or $LNi^{III}{-}X_2$ complexes, where X is a stabilizing ligand that is usually an anion, are known to have the low-spin electronic configuration.[18]

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Effects of ππ Interaction on the Electronic Properties of Asymmetrical Lanthanide Porphyrin Sandwich Complexes

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Closely spaced porphyrinic macrocycles play important roles in such diverse systems as photosynthetic proteins[1] and organic conductors.[2] For example, the primary electron donor in the photosynthetic reaction center is comprised of a special pair (SP) of bacteriochlorophyll molecules.[3-5] The electronic interactions between the molecules that comprise the SP result in characteristic features such as a long-wavelength absorption in the neutral SP and a near-infrared (near-IR) absorption in the cation SP$^+$.[1c,d] One class of model systems that mimics these optical features of SP and SP$^+$ is the lanthanide and actinide porphyrin sandwich complexes [metal(porphyrin)$_2$].[6-9] In these complexes, the electronic interactions between the porphyrin π systems are extremely strong.[8,9] We have recently proposed a molecular orbital model for the sandwich dimers that accounts for the near-IR absorption band observed in the cation radicals and provides insight into the possible nature of the additional features observed in the optical spectra of the neutral compounds.[9a,b]

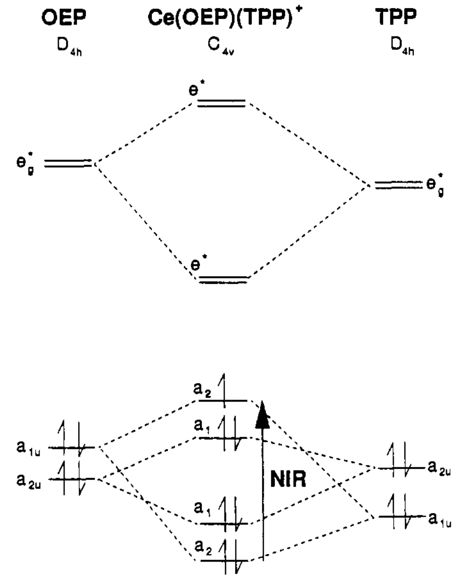

Figure 1. Partial molecular orbital diagram for Ce(OEP)(TPP)$^+$. The intradimer electronic transition that gives rise to the near-IR absorption involves promotion of an electron from an a_2 (bonding) to a_2 (antibonding) orbital and is labeled accordingly. The relative energies of the various monomer and dimer orbitals are not known; consequently, those shown in the figure were chosen for pictorial clarity only and are not to scale.

Most of the lanthanide and actinide sandwich porphyrins that have been synthesized thus far are symmetrical; that is, the two porphyrin rings are identical.[6a-f,7] In cation radicals of these complexes, the strong ππ interactions result in complete delocalization of the hole over the two porphyrin rings.[9] Recently, Holten and co-workers[8b] and Buchler and co-workers[6g,h] each reported the preparation and properties of an asymmetrical

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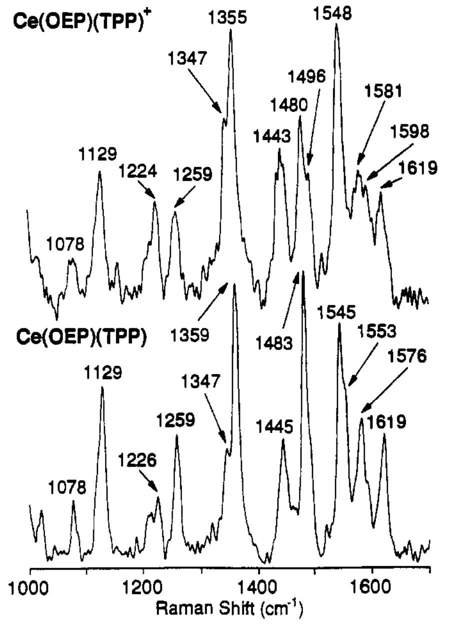

Figure 2. High-frequency regions of the B-state excitation (λ_{ex} = 363.8 nm) RR spectra of Ce(OEP)(TPP) and Ce(OEP)(TPP)$^+$ in Na_2SO_4 pellets.

complex, Ce(OEP)(TTP) and Ce(OEP)(TPP), respectively (OEP = octaethylporphyrin; TTP = tetratolylporphyrin; TPP = tetraphenylporphyrin). The electronic and redox properties of asymmetrical dimers are of interest inasmuch as photosynthetic reaction centers have recently been genetically modified such that one of the two bacteriochlorophyll molecules in the SP is replaced by a bacteriopheophytin.[10] In systems such as Ce(OEP)(TPP)$^+$, characteristic IR marker bands[11] are observed which indicate that the hole preferentially resides on the OEP ring.[6g,h] This result is readily rationalized in terms of the oxidation potentials of monomeric metallo–OEP versus metallo–TPP complexes.[12] However, the oxidation potential of Ce(OEP)(TPP)[6g] is approximately 200 mV cathodic of metallo–OEP monomers. In addition, a near-IR absorption band is observed for Ce(OEP)(TPP)$^+$. Both the cathodic shift of the redox potential and the appearance of a near-IR absorption feature indicate that $\pi\pi$ interactions significantly perturb the electronic structure of the asymmetrical sandwich compared with either metallo–OEP or metallo–TPP monomers.[8,9] Both of these properties can be accounted for in terms of the molecular orbital diagram shown in Figure 1 (vide infra). A detailed discussion of the general features of this molecular orbital scheme as it pertains to symmetrical sandwiches can be found in ref 9a,b.

The fact that strong $\pi\pi$ interactions are manifested in the redox and optical properties of Ce(OEP)(TPP) indicates that oxidation does not occur exclusively from an OEP-based molecular orbital. Instead, the electron is removed from a dimer molecular orbital whose composition is determined by the relative energies of the OEP and TPP monomer orbitals of appropriate symmetry and by the interaction between them.[9] Inspection of Figure 1 reveals that the redox orbital should be derived from the a_{1u}-like monomer orbitals of OEP and TPP. These orbitals also form the redox orbital in the symmetrical sandwich $Ce(OEP)_2$.[9a,b] In contrast, the redox orbitals of $Ce(TPP)_2$ are derived from a_{2u}-like monomer orbitals.[9a,c] The $\pi\pi$-interaction-induced redox orbital reversal that occurs in Ce(OEP)(TPP) relative to $Ce(TPP)_2$ should be directly manifested in the oxidation-induced shifts of the porphyrin skeletal vibrations. In order to probe this effect, we have examined the resonance Raman (RR) spectra of Ce(OEP)(TPP) and Ce(OEP)(TPP)$^+$. These data provide further insight into the electronic structure of asymmetrical porphyrin sandwich complexes.

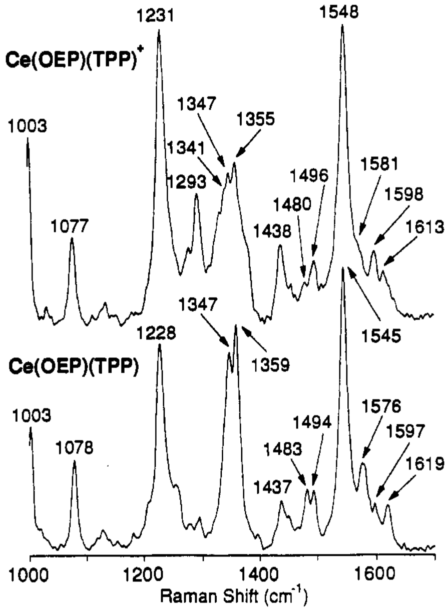

Figure 3. High-frequency regions of the B-state excitation (λ_{ex} = 406.7 nm) RR spectra of Ce(OEP)(TPP) and Ce(OEP)(TPP)$^+$ in Na_2SO_4 pellets.

Table I. Resonance Raman Frequencies (cm^{-1}) of the Ce(OEP)(TPP) and Ce(OEP)(TPP)$^+$ Complexes

	RR freq				$\Delta\nu$			
	Ce(OEP)-(TPP)		Ce(OEP)-(TPP)$^+$		OEP		TPP	
	OEP	TPP	OEP	TPP	$\Delta\nu_{SYM}$[a]	$\Delta\nu_{ASYM}$	$\Delta\nu_{SYM}$[b]	$\Delta\nu_{ASYM}$
ν_4	1378[c]	1347	1355	1341	−13	−23	−13	−6
ν_{11}	1553	1494	1581	1496	+24	+28	−10[d]	+2
ν_2	1576	1545	1598	1548	+13	+22	−8	+3

[a] Taken from ref 9a. [b] Taken from ref 9c. [c] Based on depolarization measurements. [d] This band appears as a weak shoulder in $Ce(TPP)_2^+$ spectrum and the assignment is tentative.

Experimental Section

The Ce(OEP)(TPP) complex was the generous gift of Drs. D. Holten and O. Bilsel. Oxidation to Ce(OEP)(TPP)$^+$ was effected with phenoxathiinylium hexachloroantimonate in 1,2-dichloroethane (Aldrich, 99+%) under an inert atmosphere.[6c,13] Purification of the cation was performed according to the procedures of Buchler and co-workers.[6b–e]

The RR spectra were acquired by using instrumentation described elsewhere.[14] The samples were dissolved in dichloromethane or suspended in compressed pellets with a supporting medium of Na_2SO_4. The incident laser power was approximately 35 mW and the spectral slit width was approximately 3 cm^{-1}.

Results

The high-frequency regions of the B-state excitation RR spectra of Ce(OEP)(TPP) are shown in the bottom traces of Figures 2 (λ_{ex} = 363.8 nm) and 3 (λ_{ex} = 406.7 nm). Comparison of the RR spectral features (band frequencies and depolarization ratios) of this complex with those of $Ce(OEP)_2$ and $Ce(TPP)_2$ allows ready identification of the skeletal modes of the two different porphyrin rings in the asymmetrical system.[9] The frequencies of several of these vibrational modes are listed in Table I. In general, the frequencies of the skeletal vibrations of the OEP and TPP rings in Ce(OEP)(TPP) are essentially identical with those of the

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analogous modes of the respective rings of the symmetrical sandwiches. This indicates that the extent of pure vibrational coupling between the macrocycles is negligible in all of the complexes. This does not imply, however, that the electronic interactions between the rings are small.

The high-frequency regions of the B-state excitation RR spectra of Ce(OEP)(TPP)$^+$ are shown in the top traces of Figures 2 and 3. Comparison of these spectra with those of the neutral complex reveals that the frequencies of certain skeletal modes of both the OEP and TPP rings are shifted upon oxidation. (It should be noted that the band observed at 1347 cm^{-1} in the spectrum of the cation corresponds to ν_{29} and is not due to ν_4 of residual unoxidized material.) The frequencies of several of these modes are compared with those of the neutral complex in Table I. In general, the oxidation-induced frequency shifts are large for skeletal vibrations of the OEP macrocycle and small for those of the TPP ring. In addition, the shifts observed for the OEP and TPP modes of the asymmetrical complex are larger and smaller, respectively, than those observed for the analogous modes of the OEP and TPP rings of the symmetrical sandwiches.[9] The oxidation-induced frequency shifts observed for all three sandwich complexes are compared in Table I. The shifts observed for Ce(OEP)$_2$ and Ce(TPP)$_2$ are labeled $\Delta\nu_{\mathrm{SYM}}$(OEP) and $\Delta\nu_{\mathrm{SYM}}$(TPP), respectively, while those observed for Ce(OEP)(TPP) are labeled $\Delta\nu_{\mathrm{ASYM}}$(OEP) and $\Delta\nu_{\mathrm{ASYM}}$(TPP).

Discussion

The observation that the oxidation-induced frequency shifts of the OEP and TPP skeletal modes in the asymmetrical sandwich are larger and smaller, respectively, than those of these vibrations in the symmetrical complexes is consistent with the notion that the electron is removed primarily from a dimer molecular orbital comprised predominantly of an OEP monomer orbital.[6g,h] The positive shifts observed for the ν_2 and ν_{11} modes of the OEP macrocycle are further consistent with this dimer redox orbital being derived from an a_{1u}-like OEP monomer orbital[15,16] as is the case for the symmetrical OEP sandwich complexes.[9a,b] On the other hand, the frequency shifts observed for the ν_2 and ν_{11} modes of the TPP ring in the asymmetrical sandwich, although relatively small, are opposite in direction from those observed for these modes in the symmetrical TPP sandwich.[9c] These shifts are also opposite to those typically observed for a_{2u} porphyrin cations such as CuTPP$^+$ [16] or Ce(TPP)$_2^+$.[9c] The positive shifts observed for ν_2 and ν_{11} modes of TPP upon oxidation of Ce(OEP)(TPP) are in the direction expected for an a_{1u}-like cation.[15,16] This supports the suggestion that strong $\pi\pi$ interactions result in redox orbital reversal for the TPP ring in Ce(OEP)(TPP) relative to Ce(TPP)$_2$ (vide supra).

There is no direct way to relate the magnitude of the oxidation-induced frequency shifts of the skeletal modes of the two porphyrins in Ce(OEP)(TPP) to the relative magnitudes of the coefficients of the redox orbital in the dimer. If the magnitudes of shifts are assumed to be directly proportional to the hole density, it might be estimated that the a_{1u} orbital of OEP contributes $\sim$80% to the dimer orbital. This value was obtained by averaging $|\Delta\nu_{\mathrm{ASYM}}/\Delta_{\mathrm{SYM}}|$ for the RR bands of OEP or TPP given in Table I. Inherent in this analysis is the assumption that the oxidation-induced shifts of the RR bands of the symmetrical dimers are half as large as those of the analogous bands of monomeric systems. This is true for some bands but not others.[9a,c] Another qualitative estimate of the orbital coefficients can be obtained by determining the eigenvectors of a two by two matrix in which the redox energies of the a_{1u} orbitals of the metallo-OEP and metallo-TPP monomers lie on the diagonal and the off-diagonal elements are adjusted to yield the 200-mV cathodic shift observed for Ce(OEP)(TPP) versus metallo-OEP monomers. Unfortunately, the energy of the a_{1u} orbitals of monomeric metallo-TPP complexes cannot be estimated from redox potentials because all of these complexes are a_{2u}-like cations.[16,17] If the a_{1u} orbital of TPP is placed 2000-3000 cm^{-1} below the a_{2u} orbital, [18] then diagonalization of the two by two matrix yields a dimer redox orbital that is 70-75% OEP-like in character. This estimate is reasonably close to that determined from the RR data considering the crude level of approximation.

The observation that strong $\pi\pi$ interactions perturb the redox orbital ordering in Ce(OEP)(TPP) suggests that the detailed character of the dimer redox orbitals in asymmetrical sandwich complexes can be manipulated with judicious choice of porphyrin ring substituent groups. For example, the oxidation potentials of monomeric metallo-tetrapentylporphyrins (TPnP) are considerably closer to those of metallo-OEP complexes than are those of metallo-TPP systems.[19] This suggests that an asymmetrical sandwich complex such as Ce(OEP)(TPnP) would have a dimer redox orbital in which the two rings contribute much more equally. Finally, the perturbation of the ground state properties of the asymmetrical sandwiches by strong $\pi\pi$ interactions suggests that the properties of the asymmetrical SP dimer in the genetically modified photosynthetic reaction centers[10] may also be subject to such perturbations. The importance of such effects will depend on the magnitude of $\pi\pi$ interactions between the molecules in the SP. This has yet to be determined.

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Theoretical Predictions and New Structures of Stacking Patterns for Cu$_n$X$_{2n}$L$_2$ Oligomers

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Psuedo-planar oligomers of the type Cu$_n$X$_{2n}$L$_2$ (X = Cl$^-$, Br$^-$; L = Cl$^-$, Br$^-$, or a neutral ligand) aggregate in the solid state thru the formation of long semicoordinate Cu···X bonds between oligomers. A variety of stacking patterns (polymorphs) are observed.[1-4] We have developed a notation to classify these patterns,[5,6] as well as a simple pictorial scheme to illustrate the stacking arrangements.[7] This classification scheme, while useful

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