

suggests that there is some interaction between the unpaired electrons of the f^2 U(IV) center and the single unpaired electron of the porphyrin radical. [(TPP)₂U][SbCl₆] in CH₂Cl₂ at –60 °C exhibits six broadened ¹H NMR signals;¹⁴ the pattern is similar to that of the unoxidized starting precursor¹ (TPP)₂U except that the pyrrole signal is shifted significantly upfield. In the diamagnetic limit (infinite temperature), the five phenyl proton signals of [(TPP)₂U][SbCl₆] collapse to the normal δ 6 to 9 ppm region while the pyrrole signal extrapolates instead to δ –14 ppm. This behavior indicates that the porphyrin π -radical cation possesses high unpaired spin density near the pyrrole protons.

The [(TPP)₂M][SbCl₆] complexes in CH₂Cl₂ exhibit very broad, intense ($\epsilon \sim 10^3$ cm^{–1} M^{–1}), featureless absorptions in the near-IR region at 1480 nm (fwhm 300 nm) and 1270 nm (fwhm 140 nm) for M = Th and U, respectively. These bands were first assigned in the analogous Ce(IV) complex to interporphyrin charge-transfer transitions;¹¹ recent resonance Raman data,¹⁶ however, show that the electron hole is delocalized over both porphyrins, which implies that this interporphyrin transition involves little charge transfer. Of interest in this context is the near-infrared transition observed in the special pair of bacteriochlorophyll-b found in the bacterial reaction center protein of *Rhodospseudomonas viridis*.^{7,8} The special pair radical cation dimer, (BChl)₂⁺, has an interplanar spacing of ≈ 3 Å and a characteristic intramolecular transition at 1300 nm.⁸ For comparison, [(TPP)₂Th][SbCl₆] has an interplanar spacing of 2.89 Å (see below) and an absorption at 1480 nm. Similar comparisons have previously been made for the lanthanide bis(porphyrinate) cations.^{11a,b}

(TPP)₂Th and [(TPP)₂Th][SbCl₆] have been structurally characterized by X-ray crystallography (Figure 1).¹⁷ While the (TPP)₂Th units in both the neutral species and the cation are generally similar, the Th–N bond distances, 2.55 (1) versus 2.52 (2) Å, and the displacement of the thorium atom from the mean N₄ plane of the porphyrinate core, 1.47 versus 1.45 Å, are slightly smaller in the cation. The structural parameters are similar to those of the half-sandwich complexes^{1,2} (TPP)UCl₂(thf) and (OEP)Th(acac)₂; the Th–N bond distances of the latter average 2.50 Å and the Th out-of-plane distance, Th–N₄, is 1.43 Å. The porphyrinate N₄ planes of [(TPP)₂Th][SbCl₆] are 2.89 Å apart with a twist angle of $\sim 30^\circ$, resulting in a distorted square antiprismatic geometry about thorium; this may be compared to the 2.75 Å interplanar spacing and a twist angle of 42° between the porphyrinate rings in the neutral species (OEP)₂Ce.^{11,18} The difference in interplanar spacing between the Th and Ce complexes reflects the smaller ionic radius¹⁹ of Ce^{IV} versus Th^{IV} and possibly the reduced steric demand of OEP versus TPP. Due to the high point symmetry of the crystallographic site (222), the two porphyrinate rings in [(TPP)₂Th][SbCl₆] are crystallographically identical, and no variations of the C–C or C–N bond lengths are apparent. We note that the porphyrinate rings in [(TPP)₂Th][SbCl₆] are close enough together to allow significant direct overlap of the two π -systems. Consistent with this, the NMR spectra suggest complete delocalization of the unpaired electron over both porphyrinate rings.

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(17) Crystal data for (TPP)₂Th·C₇H₈ ($T = 25$ °C): space group $I2/a$, $a = 15.377$ (4) Å, $b = 31.119$ (6) Å, $c = 15.378$ (3) Å, $\beta = 90.59$ (2)°, $V = 7358$ (5) Å³, $Z = 4$, $R_F = 5.4\%$, $R_{wF} = 6.9\%$ on 333 variables and 3646 unique data with $I > 2.58\sigma(I)$. Crystal data for [(TPP)₂Th][SbCl₆]·2C₇H₈·CH₂Cl₂ ($T = 25$ °C): space group $P4/nnc$, with $a = 19.104$ (3) Å, $c = 26.335$ (3) Å, $V = 9612$ (4) Å³, $Z = 4$, $R_F = 6.5\%$, $R_{wF} = 10.6\%$ on 248 variables and 1894 unique data with $I > 2.58\sigma(I)$. All non-hydrogen atoms except those of the solvate molecules were refined with independent anisotropic thermal parameters. The refinement of [(TPP)₂Th][SbCl₆] was complicated by the presence of disordered solvate molecules; however, the structural parameters of the [(TPP)₂Th] cation are well defined.

(18) For the related bis(phthalocyanine) derivatives of Th and U, see: (a) Lux, F.; Dempf, D.; Graw, D. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 819–820. (b) Gieren, A.; Hoppe, W. *J. Chem. Soc., Chem. Commun.* **1971**, 413–414. (c) Kirin, I. S.; Kolyadin, A. B.; Lychev, A. A. *J. Struct. Chem. (Engl. Trans.)* **1974**, *15*, 415–418.

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Preliminary spectroscopic characterization of the bis(porphyrin) dications [(TPP)₂M][SbCl₆]₂ (M = Th, U) has also been completed.²⁰ These compounds are prepared in the same fashion as the monocations but with the use of 2 equiv of (C₁₂H₈SO)SbCl₆. The complexes possess intense near-infrared bands at 1080 nm (M = Th) and 990 nm (M = U), and spectroscopic data are consistent with a bis[porphyrin π -radical cation] formulation. Further characterization of the magnetic coupling present in these bis(porphyrinato)metal systems is underway.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and complete bond distances and angles for (TPP)₂Th and [(TPP)₂Th][SbCl₆] (8 pages); tables of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

(20) Anal. Calcd for [(TPP)₂Th][SbCl₆]₂·2CH₂Cl₂: C, 47.1; H, 2.6; N, 4.9; Th, 10.1; Sb, 10.6; Cl, 24.7. Found: C, 47.1; H, 2.7; N, 4.8; Th, 9.6; Sb, 10.1; Cl, 25.0. UV–vis near infrared (CH₃CN, 25 °C) 399 (Soret), 480, 549, 608, 1080 nm; ¹H NMR (CD₃CN, 18 °C) δ 7.55, 7.47, 7.37 (m, $I_{rel} = 3$), 6.98 (s, fwhm = 30 Hz, $I_{rel} = 1$), 6.30 (s, fwhm = 28 Hz, $I_{rel} = 1$); IR (Nujol) 1285, 1267 cm^{–1}. Anal. Calcd for [(TPP)₂U][SbCl₆]₂·2CH₂Cl₂: C, 47.0; H, 2.6; N, 4.9; U, 10.3; Sb, 10.6; Cl, 24.6. Found: C, 46.5; H, 2.5; N, 4.7; U, 10.2; Sb, 10.9; Cl, 24.0. UV–vis near infrared (CH₃CN, 25 °C) 396 (Soret), 990 nm; ¹H NMR (CD₃CN, 20 °C) δ 8.40 (s, fwhm = 19 Hz, o-H), 7.56 (s, fwhm = 18 Hz, m-H), 5.95 (s, fwhm = 14 Hz, p-H), 4.88 (s, fwhm = 32 Hz, m-H), 4.15 (s, fwhm = 93 Hz, pyrrole-H), –1.73 (s, fwhm = 23 Hz, o-H); IR (Nujol) 1295, 1287, 1269 cm^{–1}.

Theory of Vibrational Circular Dichroism: *trans*-2,3-Dideuteriooxirane

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We have recently developed^{1–3} and implemented^{3–10} an a priori theory of vibrational rotational strengths and vibrational circular dichroism (VCD) spectra. To date, comparisons of this theory with experimental VCD spectra have been limited by the paucity

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Table I. Dipole and Rotational Strengths for *S,S*-*trans*-2,3-Dideuteriooxirane

mode	ν (cm ⁻¹)	D^a	R^b	$R(\vec{P}\cdot\vec{M})$	$R(\vec{P}\cdot\vec{L})$
B, C-H stretch	3042	56.5	30.7	26.0	4.8
A, C-H stretch	3037	8.9	-26.7	-22.0	-4.7
A, C-D stretch	2238	10.6	14.4	10.1	4.3
B, C-D stretch	2225	51.1	-14.8	-11.2	-3.7

^a 10⁻⁴⁰ esu² cm². ^b 10⁻⁴⁴ esu² cm².

Table II. Calculated and Observed Absorption and Circular Dichroism of *S,S*-*trans*-2,3-Dideuteriooxirane

ν_{\max}^d (cm ⁻¹)	A_{\max}	$10^5 \Delta A_{\max}$	$10^5 \Delta A_{\min}$
Calculated ^{a,b}			
3041	0.19	1.1	-0.4
2225	0.20	1.5	-1.6
Observed ^c			
3022	0.19	1.2	-0.5
2237	0.13	1.1	-1.0

^a See Figure 1. ^b Note that $\Delta A_{\max}:\Delta A_{\min}$ is not equal to (and can differ significantly from) the ratio of the positive and negative R values. ^c Reference 11. ^d Frequency at which $A = A_{\max}$.

of data for chiral molecules possessing well-defined geometries and unambiguously assigned vibrational spectra. A thorough comparison has so far been carried out only in the case of propylene oxide (epoxypropane).^{5,10} Preliminary studies have been reported for *trans*-1,2-dideuteriocyclobutane⁵ and *trans*-1,2-dicyanocyclopropane.⁷

Very recently, VCD data have been reported in this journal¹¹ for the C-H and C-D stretching transitions of *trans*-2,3-dideuteriooxirane (**1**). Fortuitously, this report coincides with the completion of extensive theoretical studies of the VCD of this molecule.¹² We here present a comparison of our most accurate calculations with the published spectra.

Calculations of vibrational dipole and rotational strengths, D and R , are carried out as described previously.⁶⁻¹⁰ Atomic polar tensors, $P_{\alpha\beta}^\lambda$, and atomic axial tensors, $M_{\alpha\beta}^\lambda$,² are calculated with analytical derivative methods and the CADPAC program.⁶ The large 6-31G (extended) basis set^{13,14} ((11s5p2d/5s2p) contracted to [4s3p2d/3s2p]) is used. $M_{\alpha\beta}^\lambda$ tensors are calculated with the distributed origin gauge.^{2,9,10} Studies reported elsewhere¹⁴ for a variety of molecules show that this basis set and gauge together give $P_{\alpha\beta}^\lambda$ and $M_{\alpha\beta}^\lambda$ tensors not far from the Hartree-Fock limit. The equilibrium geometry, \vec{R}_0 , is the (r_m) experimental geometry of Hirose.¹⁵ The vibrational force field is a scaled quantum mechanical (SQM) force field^{16,17} derived by scaling a 6-31G (extended) force field, calculated at \vec{R}_0 with CADPAC, to fit 20 unambiguously assigned frequencies of gaseous oxirane and 2,2,3,3-tetradeuteriooxirane.¹⁸ The RMS deviation of theoretical and experimental frequencies is 12 cm⁻¹. The calculated frequencies and D and R values of the C-H and C-D stretching transitions of the *S,S* enantiomer of **1** are given in Table I.

The absorption and the VCD of the two C-H stretching transitions and of the two C-D stretching transitions of **1** are unresolved in the CCl₄ solution spectra,¹¹ and deconvolution of the data was not reported. We have therefore synthesized absorption and VCD spectra from our calculations, assuming Lorentzian line shapes.¹⁰ Line widths are assumed to be identical

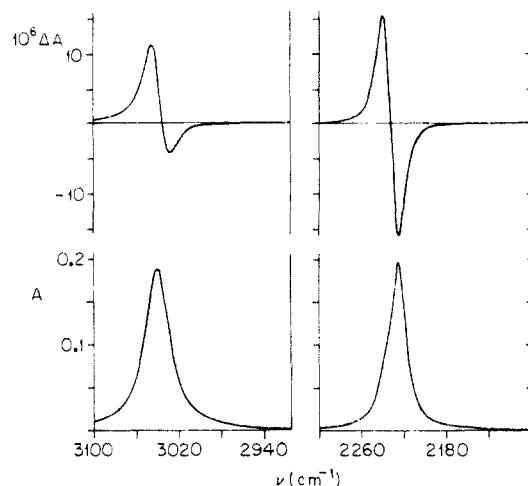


Figure 1. Absorption and VCD spectra, calculated from the ν , D , and R values in Table I, assuming Lorentzian line shapes.¹⁰ Equal line widths are assumed for the A and B C-H stretching and the A and B C-D stretching transitions. Line widths are chosen to reproduce the width at half-height of the observed absorption¹¹ (28 and 20 cm⁻¹ for the C-H and C-D stretching bands, respectively). A_{\max} for the C-H stretching transition is normalized to the observed A_{\max} .¹¹

for overlapping transitions and are chosen to reproduce the observed band widths at half-height. The results are shown in Figure 1. Since the solution concentration was not reported, the peak absorbance in the C-H stretching region is normalized to the experimental value.

The general features of the observed absorption and VCD spectra,¹¹ including the bisignate nature of the VCD spectra in both C-H and C-D stretching regions, are correctly predicted. The quantitative agreement is also good, as detailed in Table II. It should be noted that the peak A and ΔA values are very sensitive both to the assumption of identical line shapes of overlapping transitions and to the specific line widths used. The agreement of theory and experiment could undoubtedly be even further improved by more precise choices of line shapes and widths.

Our calculations do not include anharmonicity. The agreement between theory and experiment suggests that anharmonicity (including Fermi resonance) is not of major importance for these transitions of **1**. A more detailed evaluation of this conclusion requires more highly resolved spectra (e.g., matrix isolation spectra).

Within the distributed origin gauge, rotational strengths are the sum of two terms, referred to as the " $\vec{P}\cdot\vec{M}$ " and " $\vec{P}\cdot\vec{L}$ " terms, respectively.² The latter term contains only $P_{\alpha\beta}^\lambda$ tensors. The approximation in which " $\vec{P}\cdot\vec{M}$ " terms are neglected is the "atomic polar tensor (APT) equation".^{2,3} The magnitudes of the " $\vec{P}\cdot\vec{M}$ " and " $\vec{P}\cdot\vec{L}$ " terms in our calculations are given in Table I. The " $\vec{P}\cdot\vec{M}$ " terms are strongly preponderant. The APT equation thus yields predictions of very poor accuracy. Since the "fixed partial charge" (FPC) and "coupled oscillator" (CO) equations³ are further approximations to the APT equation,² it follows that the FPC and CO equations are of even lower accuracy. Our results support the conclusion that the APT, FPC, and CO equations do not provide a generally reliable basis for the interpretation of VCD spectra.

A theory providing reliable prediction of VCD spectra can in turn be used in the interpretation of experimental VCD spectra of molecules of unknown stereochemistry. The present work further supports the conclusion that such a theory now exists. Its successful application to *trans*-2,3-dideuteriooxirane further demonstrates the particular potential utility of VCD in the characterization of molecules whose chirality originates solely from the substitution of H by D.

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