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Ground-State and Optical Spectrum of Metallophthalocyanine Radical Anions from Low-Temperature Magnetic Circular Dichroism Spectroscopy

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There is considerable current interest in the spectral properties of the anion-radical species of metal porphyrin and phthalocyanine (Pc) complexes.[1-12] Metal porphyrins and phthalocyanines are aromatic, 18-π-electron systems. Intense bands near 350 and 670 nm in the absorption spectrum of neutral phthalocyanines can be explained in terms of three allowed, x/y-polarized π–π^* transitions within the LCAO model developed by Gouterman.[13] The optical data for neutral and ring-oxidized radical-cation species are well-known. We have previously used Gouterman's model as the basis for band assignments of the absorption spectra of the ring-oxidized cation-radical complexes [MgPc(–1)]·⁺, [ZnPc(–1)]·⁺ and [Co^IIIOEP(–1)]·²⁺,[14-19] based on assignments of the absorption and MCD spectra of neutral MPc(–2) species.[19a] However, despite many experimental studies,[20-24] the optical

spectra of the ring-reduced, anion-radical species are not well established, and band assignments for these optical spectra have not been described previously. An important first step in the assignment of the bands observed for anion-radical complexes is to establish the degeneracy of the ground and excited states of the ring-reduced molecule.[13]

Magnetic circular dichroism (MCD) spectra have previously provided essential information about ground and excited states for both neutral and ring-oxidized cation-radical complexes of metallophthalocyanines and metalloporphyrins.[14-19] In this paper, we report the first MCD spectrum obtained for a species generated electrochemically in situ in the sample bore of a superconducting magnet and the first low-temperature MCD spectrum for an anion radical of either a phthalocyanine or porphyrin complex. Analysis of these MCD spectral data enables us to extend our earlier assignment of MgPc(–2) and its radical cation to the radical anion. The MCD data provide direct evidence that the ground state of [Mg^IIPc(–3)]·⁻ is subject to a Jahn–Teller distortion and is hence orbitally nondegenerate.

The specificity of the MCD technique arises from three highly characteristic spectral features, the *A*, *B*, and *C* terms.[25] The derivative-shaped *A* term is temperature independent and identifies degenerate excited states, while the Gaussian-shaped *C* term is highly temperature dependent and identifies an orbitally degenerate ground state.[25] Although not normally of as much utility in the assignment of spectral data of symmetric molecules, the signs of *B* terms that arise from mixing between closely related states with x or y polarization can provide definitive data on the structure of the excited states.[26] In this paper, we use the signs of a series of *B* terms that arise from coupled pairs of degenerate states split by the Jahn–Teller effect to characterize the spectrum of the phthalocyanine π anion radical.

MgPc provides a suitable starting point for a general study of metallophthalocyanine anion radicals because the complex has D_{4h} symmetry and redox reactions involve only the ligating ring. Several sets of spectral data have previously been reported for [MgPc(–3)]·⁻ (the anion radical of MgPc), including absorption band maxima and EPR signals for chemically and electrochemically generated species by Clack and Yandle[20] and preliminary absorption and MCD spectra for the chemically reduced [MgPc]^n⁻ (*n* = 1–4) species by Lindler et al.[21] EPR studies on [MgPc(–3)]·⁻ at 77 K indicate that the species is monomeric,[21,22-24] unlike the diamagnetic dimer of radical cations that forms at low temperatures.[17]

Experimental Section

Reduction of the ring was carried out in thin-layer spectroelectrochemical cells with designs based on those described by Lever.[27-28] MgPc was synthesized as previously described with a variety of axial ligands.[29-31] Although axial ligation appears to have an effect on the stability of the anion in solution, no major spectral differences have been seen. The initial reduction of [MgPc(–2)] results in a blue shift of the 670-nm band, which is probably caused by the loss of axial ligands.[19b] Initial phthalocyanine concentrations were typically in the 10⁻⁴ M range. Spectrophotometric grade dimethylformamide (DMF) and dimethylacetamide (DMA) were used as solvents, and tetrapropylammonium perchlorate (TPAP) was used as the supporting electrolyte. The reduction was carried out under the control of a Princeton Applied Research 273 potentiostat/galvanostat. Fixed currents, typically in the 0.1–1.0-μA range, were applied across the spectroelectrochemical cell. [MgPc(–3)]·⁻ can be formed reversibly with isosbestic spectral changes in the absorption spectrum.[19b] Solutions for low-temperature MCD and absorption

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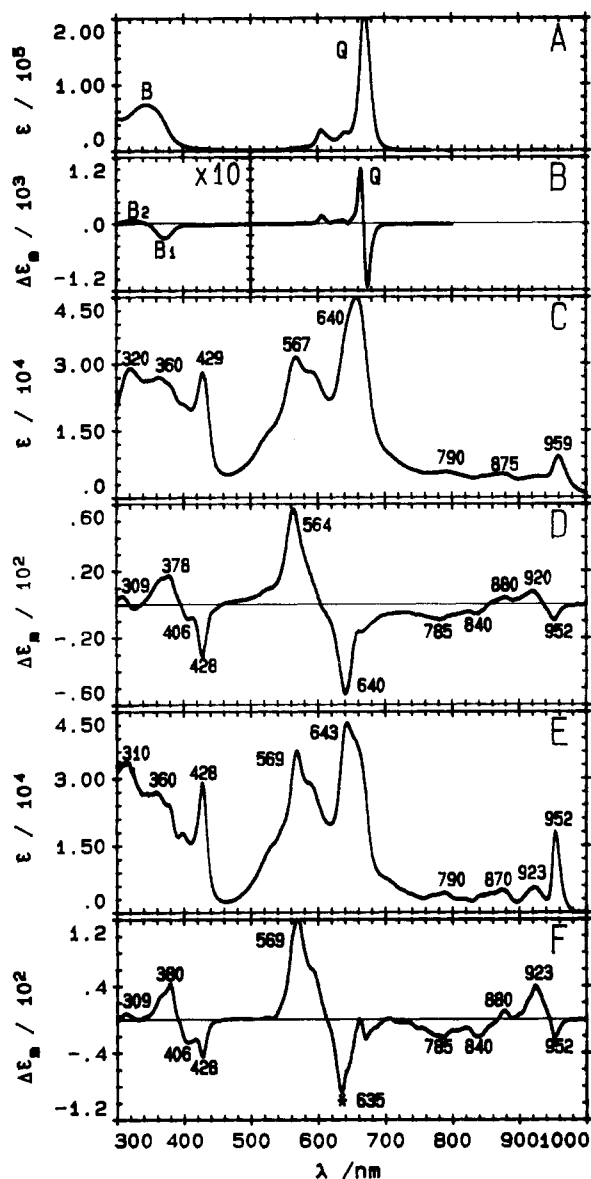
Figure 1. Absorption (A/C/E) and MCD (B/D/F) spectra of MgPc-(-2) (A/B) and [MgPc(-3)]⁻ at room (C/D) and low temperature (E/F): (A) absorption spectrum of MgPc in dimethylformamide; (B) MCD spectrum of MgPc in dimethylformamide; (C) absorption spectrum of [MgPc(-3)]⁻ recorded at 298 K by reduction of a solution of MgPc(piperidine)₂/DMF/0.1 M TPAP; (D) MCD spectrum of [MgPc(-3)]⁻ measured at 298 K by reduction of MgPc(quinoline)₂/DMF/0.1 M TPAP; (E) absorption spectrum of [MgPc(-3)]⁻ recorded at 77 K as a frozen glass (anion obtained by reduction of MgPc(quinoline)₂/DMF-DMA/0.05 M TPAP); (F) MCD spectrum of [MgPc(-3)]⁻ at 2.8 K formed by reduction of MgPc(quinoline)₂/DMF-DMA/0.1 M TPAP (the shoulder at 645 nm on the negative MCD band is an artifact of the measurement and contributes to a low value for the peak maximum (indicated by *635)).

spectra were reduced electrochemically at approximately 190 K in a DMF–DMA solvent mixture and were vitrified in liquid nitrogen prior to spectral measurement.

Room-temperature MCD spectra were recorded using an Oxford Instruments SM2 superconducting magnet located in the sample compartment of a Jasco J-500 spectropolarimeter under the remote control of an upgraded version of the CDSCAN computer program.[28,32] As phthalocyanine anion radicals are highly reactive, the magnet bore was maintained under an inert-gas atmosphere. The field strength and sign were calibrated by using the visible-region band of aqueous CoSO4 ($\Delta\epsilon_m$ = -1.9 × 10⁻² L mol⁻¹ cm⁻¹ T⁻¹ at 510 nm). Room-temperature absorption spectra were measured with an Aviv 17DS spectrophotometer

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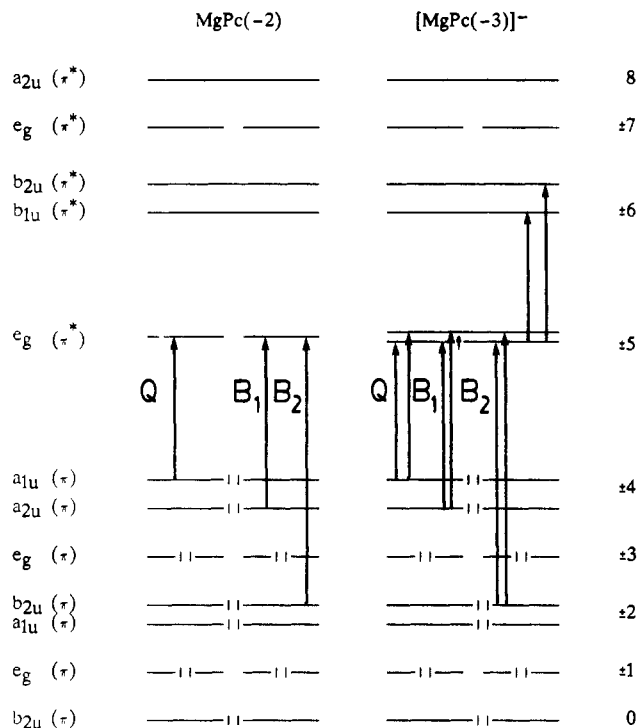

Figure 2. Molecular orbitals involved in the major absorption transitions with energies between 10 000 and 50 000 cm⁻¹ adapted from Minor, Gouterman, and Lever.[34] The order of the orbitals is based on theoretical models for the [MgPc(-2)] and [MgPc(-1)]⁺ species.[13,26,34] No account has been taken of changes in the energies of the molecular orbitals as a result of the different ring occupation upon reduction. The transitions shown are those anticipated through application of Gouterman's four-orbital LCAO model.[13] The association of orbital angular momentum with pairs of states follows from the interpretation of the molecular orbitals of an aromatic molecule in terms of the sequence 0, ±1, ±2, etc.[26] The arrows indicate transitions that give rise to bands observed in the 300–900-nm region of the absorption and MCD spectra.

(a spectrometer based on the Cary 17 monochromator) using the supplied software package. An SM4 superconducting magnet was used for liquid-helium-temperature MCD spectroscopy. Liquid-nitrogen-temperature absorption spectra were recorded using an Oxford Instruments Model 204 optical cryostat. Spectra Manager was employed for spectral data manipulation, analysis, and plotting.[33]

Results and Discussion

The MCD spectrum of MgPc(-2) (Figure 1B) is characterized by *A* terms that arise from a series of *x,y*-polarized transitions (¹A₁g → ¹Eᵤ) of the D_{4h} 18-π-electron ring (see Figure 2). The individual bands are known as Q, B₁, and B₂, increasing in energy from 670 to 270 nm.[14-18] Initial application of Gouterman's theory predicts that the ground-state configuration for [MgPc(-3)]⁻ will be (a₂ᵤ)²(a₁ᵤ)²(eg*)¹.[13] The resulting ²Eg state would be orbitally degenerate (Figure 2). If the angular momentum continues to increase at the higher orbital as shown in Figure 2, the eg* orbital will have ±5 units. With this configuration, only temperature-independent Faraday *B* terms and temperature-dependent Faraday *C* terms would be expected from the allowed π–π* and π*–π* transitions that transform as ²Eg → ²A₁/₂ᵤ or ²B₁/₂ᵤ.[14-18]

There is, however, no significant temperature dependence in the MCD spectrum of [MgPc(-3)]⁻ recorded between room temperature and cryogenic temperatures (Figure 1C–F). The minor differences in the MCD spectra can be explained in terms of the slight band sharpening seen at 77 K in the corresponding absorption spectra. The lack of temperature dependence unambiguously identifies an orbitally nondegenerate ground state. *C* terms exhibit a strong 1/kT temperature dependence, so the discrepancy between the extinction coefficients seen in Figure 1D,F is negligible.[25]

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Table I. Major Band Centers in the Absorption (77 K) and MCD (2.8 K) Spectra of [MgPc(-3)]˙⁻

						wavelength/nm (MCD sign)					
abs	360		428	569	643	790	855			923	952
MCD	380(+)	406(−)	428(−)	569(+)	[635](−)	785(−)	840(−)	880(+)		923(+)	952(−)

Table II. Splitting Energy between ± Pairs of Bands in the MCD (2.8 K) and Absorption (77 K) Spectra of [MgPc(-3)]˙⁻

	range/nm	MCD band pair/nm	energy diff/cm⁻¹
set i	300–450	380–428	2950
set ii	500–700	569–643	2050
set iii	850–1000	923–952	330

The absorption and MCD spectra shown in Figure 1C–F are quite unusual when compared with spectra of other metallophthalocyanines.[19a] The absence of derivative-shaped A terms contrasts with the strong A terms which dominate the spectra of MgPc(-2) (Figure 1B) and the π-cation-radical [MgPc(-1)]˙⁺ species.[16,17] The band centers are summarized in Table I. It should be noted that the shoulder near 670 nm in the absorption spectrum and the weak positive A term in the MCD spectrum are due to minor fractions of the extremely intense Q band ($\epsilon \sim$ 200 000) of MgPc(-2). The spectrum of the anion radical is therefore composed entirely of B terms. We note that this means that, with a nondegenerate ground state, each excited state is also nondegenerate (Figure 2). A recurring spectral feature centered on 950, 640, and 430 nm can be seen that involves pairs of oppositely signed B terms. The overall features can therefore tentatively be identified as three series of transitions (based on a ± sequence in the MCD spectrum) that make up the bands seen between (i) 300 and 450 nm, (ii) 500 and 700 nm, and (iii) 850 and 1000 nm.

The π–π* transitions of metallophthalocyanines are usually explained in terms of a 16-membered cyclic polyene containing 18 electrons.[13,26] The electronic structure of an ideal cyclic polyene would contain orbitals with 0, ±1, ±2, ..., ±7, 8 orbital angular momentum units. The four-electron LCAO model of Gouterman has been successful in predicting the spectra that arise when the ring is distorted by the addition of aza linkages of the phthalocyanine dianion ligand, which is predicted to lift the degeneracy of each ungerade, degenerate orbital.

The lifting of the orbital degeneracy of e_g^* is probably caused by a Jahn–Teller splitting of the anticipated ^2E_g ground state. Minor et al.[34] used a similar argument to explain the lack of EPR signal for [MgPc(-4)]²⁻, a species which would be expected to have a $^3A_{2g}$ ground state. Transitions into closely linked Jahn–Teller-split states can be expected to give rise to coupled pairs of oppositely signed B terms similar to those which dominate the MCD spectrum.[26] For pairs of states, which are relatively isolated, the resulting MCD B terms will be x and y polarized and will sum to zero.[25,26] The separation of these bands will be determined by the splitting of the orbitals.

The splitting between each ± pair in the MCD spectrum is different, ranging from 330 to 2950 cm⁻¹ (Table II). We tentatively associate bands between 300 and 450 nm (388/428 nm) and between 850 and 1000 nm (923/952 nm) as belonging to a set characterized by narrow, unsplit bands, followed by lower intensity bands. The band system at 569/635 nm, which is characterized by two pairs of oppositely signed B terms, appears to belong to a second set. We suggest that the bands in the first set arise from π–π* transitions into the Jahn–Teller-split e_g^* orbital, which represent the original Q and B_1/B_2 bands. The 923/952-nm splitting of 330 cm⁻¹ then may represent Jahn–Teller splitting of the e_g^* orbital. We think that the band system in the 300–450-nm region is more complex and comprises both π–π* (the B_1 and B_2 bands) and π*–π* bands. The 569/643-nm bands probably arise from transitions out of the split e_g^* into the b_{1u}^* and b_{2u}^* orbitals (see Figure 1). The 2050-cm⁻¹ split would

therefore represent the energy difference between b_{1u}^* and b_{2u}^*. Our rationale for these choices of orbitals is as follows. (i) The 923/952-nm bands and the 388/428-nm bands exhibit very narrow bandwidths, with apparent vibrational bands lying to higher energy, much like the Q band shown for MgPc in Figure 1A. (ii) We associate the larger extinction coefficients at 569 and 643 nm with transitions out of the e_g^* orbital into b_{1u}^* and b_{2u}^* orbitals that are reportedly significantly split in neutral complexes.[13] (iii) We assume a general red shift of the MPc(-2) spectrum of about 4500 cm⁻¹ is associated with ring reduction.

In summary, room- and low-temperature MCD spectroscopies have provided valuable information unavailable from absorption spectra alone. These data provide unambiguous evidence that the ground and excited states of [MgPc(-3)]⁻ are nondegenerate.

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Treatment of Vitamin B₁₂ and Aquocobalamin (B₁₂ₐ) with the Efficient Hydrolytic Agent [Co(trpn)(H₂O)₂]³⁺

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Introduction

Considerable effort has been expended recently on promoting the hydrolysis of phosphate esters because of the utility of phosphodiester hydrolysis reactions in probing DNA and RNA sequences and structure.[1] However, another phosphodiester group of biochemical interest exists in B₁₂ compounds. Here, the phosphodiester group forms part of the linkage between the axial 5,6-dimethylbenzimidazole group and the equatorial corrin ring (Chart I, which also gives the IUPAC atom numbering scheme). Cleavage of this group requires rather drastic conditions, but the resulting cobinamides are very useful for understanding the role of steric effects on the B₁₂ cofactor during the Co–C bond homolysis step in enzymic processes.[2] A milder cleaving agent would thus be very useful for the preparation of cobinamides.

One of the most effective agents promoting phosphodiester hydrolysis is the complex [Co(trpn)(H₂O)₂]³⁺ (trpn = tris-(3-aminopropyl)amine) studied primarily by Chin and co-workers.[3–6] Therefore, we have probed the potential utility of this promising

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