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# Excited-State Spectra and Lifetimes for Oxomethoxomolybdenum(V) Tetraphenylporphine: A Comparison of $d^1$ and $d^9$ Metalloporphyrin Photophysics[1]

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The $d^1$ metalloporphyrin oxomethoxomolybdenum(V) tetraphenylporphine [OMo(TPP)OCH$_3$] was studied in tetrahydrofuran by picosecond absorption spectroscopy using a double-beam mode-locked Nd:glass laser system delivering 6-ps (fwhm) pulses at 527 nm with 1–2 mJ/pulse. Change in absorbance ($\Delta A$) spectra were recorded from the time of photoexcitation to 5 ns after excitation in the 580–740-nm region. Two transient species were observed with lifetimes of 2–9 ps and 4 ± 1 ns. The first relaxation is assigned to the establishment of the [$^4T_1(\pi,\pi^*) \rightleftharpoons {}^2T_1(\pi,\pi^*)$] equilibrium and the second to the radiationless decay of the [$^4T_1(\pi,\pi^*) \rightleftharpoons {}^2T_1(\pi,\pi^*)$] equilibrium of states. The initially populated $^2S_1(\pi,\pi^*)$ state is known to be emissionless in Mo(V) porphyrins and was not observed, $\tau < 2$ ps. These results and assignments are then compared with those of other $S = {}^1/_2$ metalloporphyrins, i.e., $d^9$ copper(II) and silver(II) porphyrins.

## Introduction

Knowledge of the photochemical and photophysical properties of metalloporphyrins is important and interesting for many reasons. These complexes can be considered as models of hemoproteins that activate molecular oxygen.[3] They can act as mediators in biochemical redox reactions,[4–6] and they can serve as precursors in the preparation of one-dimensional electrical conductors.[7] The fact that metalloporphyrins absorb light strongly in the visible and often in the near-infrared spectral regions suggests them as choice candidates for the role of photosensitizer in light-harvesting systems for solar energy conversion and storage.[8–10] Recent studies have also shown that cofacially joined metalloporphyrins and free-base porphyrins can serve as functioning models of the primary electron-transfer couple of photosystem II of green plants.[11,12]

The effect of the central metal on excited-state relaxations in metalloporphyrins has been the subject of both theoretical[8] and experimental studies.[11–16] Rentzepis and co-workers[17]

have shown that the central iron atom plays a predominant role in the electronic energy relaxation processes of iron(II) porphyrins. These complexes decay nonradiatively, most likely through low-lying ligand-field (LF) states. Recent work has examined the photophysical consequences of varying the axial ligands (L) in osmium(II) porphyrins.[18] For these metalloporphyrins the choice of axial ligand determines whether the lowest energy excited state is $(\pi,\pi^*)$ or $(d,\pi^*)$.[8,18]

The object of this study was to compare the electronic relaxation processes in a typical molybdenum(V) $d^1$ porphyrin with those of related $S = {}^1/_2$ metalloporphyrins. The chemistry of the early transition metals in high oxidation states such as niobium(V), tungsten(V), rhenium(V), and molybdenum(V) is dominated by the presence of very strong O=M [M = metal] bonding.[19–23] Thus we chose to study (5,10,15,20-tetraphenylporphinato)oxomethoxomolybdenum(V) [OMo(TPP)OCH$_3$] and compare it to previously studied copper(II) and silver(II) $d^9$ porphyrins.

## Experimental Description

OMo(TPP)OCH$_3$ was available from an earlier study.[24] All other chemicals were of reagent grade or spectral quality and were used without further purification. The picosecond absorbance measurements were made on a double-beam, mode-locked Nd:glass laser system[25,26] delivering 6-ps pulses (fwhm) at 527 nm with 1–2 mJ/pulse. The laser system used a SIT-vidicon detector coupled to an OMA-2 optical multichannel analyzer (EG&G PARCO). Complete details of the data acquisition procedure have been described elsewhere.[18,26,27]

Initial work was done on a degassed sample of the porphyrin complex in dichloromethane. However, some irreversible photochemistry occurred after ~50 laser shots. Photodecomposition also occurred in 4:1 v/v CH$_2$Cl$_2$/CH$_3$OH. We had earlier observed similar photodecomposition of a bis(trimethyl phosphite)osmium(II) porphyrin in chlorinated solvents, so this behavior should not be taken as ex-

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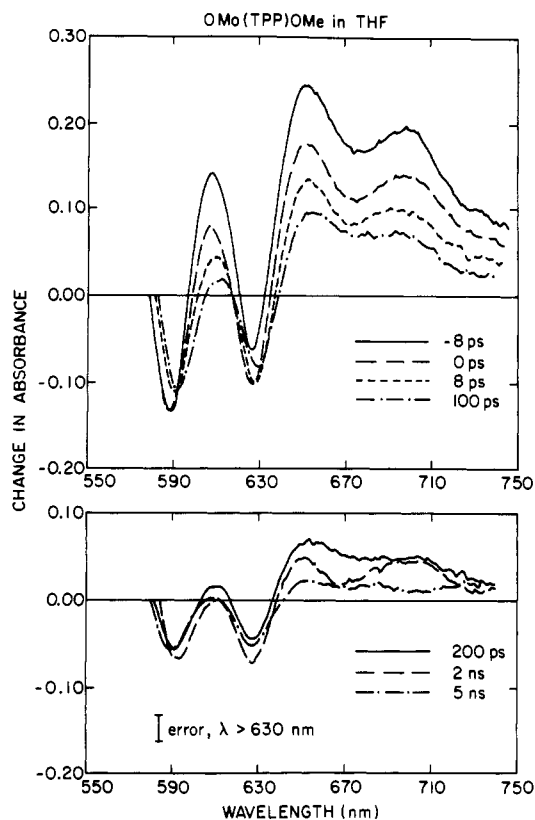
**Figure 1.** Change in absorbance ($\Delta A$) vs. wavelength plots for the indicated times following photoexcitation of OMo(TPP)OCH$_3$ in THF. $\Delta A$ spectra for times less than or equal to 100 ps are displayed in the top panel and those for times longer than 100 ps in the bottom panel. See the text for experimental details.



**Figure 2.** Kinetic plots of ln ($\Delta A$) vs. time for OMo(TPP)OCH$_3$ in THF at 650 nm. The experimental conditions are the same as in Figure 1. The solid lines are calculated fits to the data for the indicated first-order lifetimes.

ceptional.[28] Ledon and Bonnet[24] have recently reported that OMo(TPP)OCH$_3$ in 5% v/v methanol/benzene solution homolytically dissociates when irradiated in the Soret band, but not when irradiated in the $\alpha$ and $\beta$ bands. The quantum yield for photohomolysis is quite small, only 0.015. Importantly, no photohomolysis occurred for OMo(TPP)OCH$_3$ in aerated tetrahydrofuran (THF) even after exposure in the Soret region to 455-nm light from a 1000-W Hg–Xe lamp for 75 min. Consequently THF was used as the solvent for the picosecond experiments. All samples were degassed by repeated freeze–pump–thaw cycles and kept in flame-sealed cells. The concentrations were (1–2) $\times$ 10$^{-4}$ M; absorbance 0.2 at 527 nm in a 2-mm path-length cell. Change in absorbance ($\Delta A$) spectra were measured in the 580–740-nm region from the time of excitation (−8–0 ps) to 5 ns after photoexcitation.

The effects of time dispersion in the white probe pulse are important for very short-lived ($\tau \le 25$ ps) excited states such as are found in the OMo(TPP)OCH$_3$ complex. Light of shorter wavelengths travels more slowly in dense media such as water and glass than does light of longer wavelengths. In our apparatus there is about 1-ps delay for every 35 nm of spectral increment in the 550–775-nm region. For optical transients with lifetimes greater than 25 ps, these delays are not significant. The procedure we have adopted is to specify the time of arrival of the longest wavelength probe light relative to the photoexcitation pulse. Negative times refer to times at which the probe pulse reached the sample before or during excitation, and positive times indicate that the probe pulse arrived at the sample after photoexcitation. To determine the arrival time of any wavelength, the relative delay at that wavelength must be added to the arrival time of the longest wavelength in the spectrum. For example, a $\Delta A$ spectrum probing the 740-nm region at 0 ps is probing the 600-nm region +4 ps after excitation.

Prior study of the ligand-to-metal charge-transfer (LMCT) states of iron(III) and osmium(III) polypyridine complexes at room temperature[29] has shown these states to be observable, but to relax on
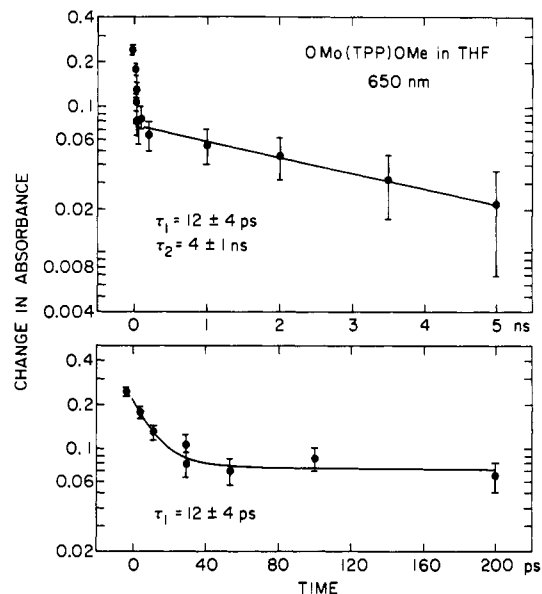
a time scale shorter than the duration of the 6-ps excitation pulse. Plots of ln ($\Delta A$) vs. time (for $t > 0$ ps) for these excited states yield apparent decay times of 9 ± 3 ps. These represent the instrumental response of our laser system, which is mainly determined by the convolution of the 6-ps excitation and 8-ps probe pulses. On the other hand, if the initially populated excited states live less than about 2 ps,[30] the excited-state populations would generally be too small to yield measurable absorbance changes. To differentiate between extremely short-lived (unobserved) excited states and those observable during but not after photolysis, we designate them in the tables and text as <2 and 2–9 ps, respectively.

**Results**

Figure 1 presents $\Delta A$ spectra for times −8 to 100 ps (upper panel) and 200 ps to 5 ns (lower panel) following photoexcitation of OMo(TPP)OCH$_3$ in THF. Ground-state bleaching (−$\Delta A$, GSB) is apparent at $\sim$590 and $\sim$630 nm where the ground-state Q bands are located; also, a broad ground-state absorption band at $\sim$645 nm ($\lambda_{max}$) may contribute to the dip in excited-state absorption (+$\Delta A$, ESA) seen in the 680-nm region. Figure 2 presents $\Delta A$ vs. time plots of these data in the 650-nm region. After 100 ps the data can be described by a first-order decay process with a lifetime of 4 ± 1 ns. At earlier times a lifetime of 12 ± 4 ps is required to fit the data. The solid lines shown in Figure 2 are the calculated first-order fits to the data. It is worth noting that while substantial decay of the initially formed ESA occurs within 100 ps of excitation at $\sim$600 nm and at wavelengths beyond 640 nm, very little decay is seen in Figure 1 in the GSB regions. This indicates that the first excited state relaxes with high yield (>50%) to a second longer lived excited state or photoproduct.

The apparent decay lifetime of 12 ± 4 ps is not distinguishable from an instrument-response-limited decay of 9 ± 3 ps. Therefore we will refer to it in subsequent sections as 2–9 ps. Similar dual-decay relaxations have been reported for osmium(II) porphyrins with lowest energy excited states that are (d,$\pi^*$) in character.[18,27] Of particular relevance are the results of Kobayashi et al.[15] for the electronically related d$^9$ porphyrins, copper(II) and silver(II) protoporphyrin IX di-

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Table I. Excited-State Lifetimes in $d^1$ and $d^9$ Metalloporphyrins at Room Temperature

| porphyrin | electronic configuration of metal | $\tau[^2S_1]$,[a] ps | $\tau[^2T_1]$,[b] ps | $\tau[^4T_1 \rightleftharpoons ^2T_1]$, ns |
|---|---|---|---|---|
| $Cu^{II}(PP\text{-}IX\text{-}DME)$[c] | $d^9$ | <2 | 450 ± 50 | >1[d] |
| $Ag^{II}(PP\text{-}IX\text{-}DME)$[c,e] | $d^9$ | <2 | 2–9 | >1 |
| $Ag^{II}(MS\text{-}IX\text{-}DME)$[f,e] | $d^9$ | <2 | 2–9 | not seen |
| $OMo(TPP)OCH_3$[e] | $d^1$ | <2 | 2–9 | 4 ± 1 |

[a] Extremely short excited-state lifetimes (for unobserved states) are denoted by <2 ps (see text).  [b] Instrument-response-limited, excited-state lifetimes (for observed states) are denoted by 2–9 ps (see text).  $\tau[^2T_1]$ Refers to the tripquartet–tripdoublet equilibration time (reaction 3).  [c] Reference 15.  [d] 94 (106) $\mu$s at 690 (725) nm at 77 K (see ref 42).  [e] No observable luminescence.  [f] Silver(II) mesoporphyrin IX dimethyl ester: ref 16.

methyl ester [$M^{II}(PP\text{-}IX\text{-}DME)$, M = Cu or Ag]. Table I compares the picosecond kinetic results of these $S = \frac{1}{2}$ complexes with that shown above for $OMo(TPP)OCH_3$.
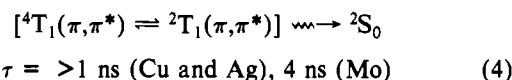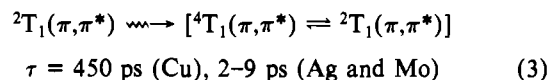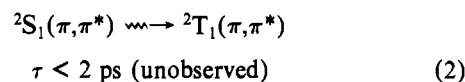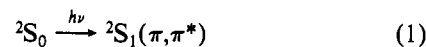
## Discussion

**Ground-State Properties of $OMo(TPP)OCH_3$.** Investigations by Matsuda et al.[7,31] have shown that while $OMo(TPP)Cl$ exists as a dimer in dichloromethane, $OMo(TPP)X$ [X = $CH_3O^-$, $CH_3COO^-$, and $ClO_4^-$] complexes are monomers. Magnetic susceptibility[32-34] and ESR[31,33-35] studies have shown that $OMo(TPP)X$ complexes contain molybdenum(V), which has a $d^1$ electronic configuration. We found the following visible absorptions in $CH_2Cl_2$ (THF): 538 (536), 580 (579), 621 (618), and 675 (645) nm. These band locations agree well with those in the literature[7,13] and provide reasonable certainty that $OMo(TPP)OCH_3$ is a monomer in THF as well as in $CH_2Cl_2$, since the absorption spectrum is known to be sensitive both to dimerization and to exchange of axial ligand X.[35-37] Additional absorption features have been reported[7] at 455 (Soret), 393 (sh) and 367 (sh) nm.

**Excited States of $OMo(TPP)OCH_3$.** $OMo(P)X$ [P = porphyrin] complexes exhibit "extra" absorptions in the UV–visible spectral regions in addition to the "normal" porphyrin $\alpha$, $\beta$, and Soret bands. Consequently Gouterman and Co-workers have classified them as d-type "hyper"-porphyrins.[8,38,39] For $OMo(OEP)OCH_3$ (OEP = octaethylporphine) Gouterman has assigned the 342-nm band (below the 443-nm Soret band) to an $a_{1u}(\pi),a_2(\pi) \rightarrow e_g(d_\pi)$ porphyrin-to-metal charge-transfer $(\pi,d_\pi)$ transition. Similarly the 393-nm band in $OMo(TPP)OCH_3$ is likely to be a $(\pi,d_\pi)$ type. However a resonance Raman study of $OMo(TPP)OCH_3$ also suggests that the $(\pi,\pi^*)$ Soret band may be substantially mixed with the nearby $(\pi,d_\pi)$ states.[40] Analogy with orbital energy calculations for vanadyl $(VO^{2+})$ porphine[41] suggests that the singly occupied $d_{xy}$ orbital in $OMo(TPP)OCH_3$ is likely to be near but above the filled $a_{1u}(\pi),a_{2u}(\pi)$ levels. In this case, $a_{1u}(\pi),a_{2u}(\pi) \rightarrow d_{xy}$ and $d_{xy} \rightarrow e_g(\pi^*)$ transitions are likely

to be lower in energy than the $a_{1u}(\pi),a_{2u}(\pi) \rightarrow e_g(\pi^*),e_g(d_\pi)$ transitions responsible for the complicated UV–visible absorption spectrum.

The lowest energy excited states of diamagnetic metalloporphyrins containing magnesium(II), zinc(II), cadmium(II), palladium(II), and mercury(II) arise from $(\pi,\pi^*)$ transitions among the porphyrin's levels and have singlet ($S_1$) and triplet ($T_1$) character. By contrast, $OMo(TPP)OCH_3$ has a $d^1$ electronic configuration and its ground state is a doublet, $^2S_0$. The unpaired electron in $d_{xy}$ interacts with the lowest energy $(\pi,\pi^*)$ excited states to create the following new states: a "singdoublet" $^2S_1(\pi,\pi^*)$, a "tripdoublet" $^2T_1(\pi,\pi^*)$, and a "tripquartet" $^4T_1(\pi,\pi^*)$.[8,14] Copper(II) and silver(II) porphyrins are analogous in that their $d^9$ electronic configurations also have one unpaired electron. In the case of copper(II) porphyrins, $^2T_1$ is only 200–700 cm$^{-1}$ higher in energy than the $^4T_1$ state.[8] Thus we can expect $(\pi,\pi^*)$ tripdoublet and tripquartet states to populate each other at room temperature if their lifetimes are sufficiently long.

**Assignments for Optical Transients.** The following decay scheme describes the likely excited-state relaxation routes in $OMo(TPP)OCH_3$ and the other in the $S = \frac{1}{2}$ metalloporphyrins that have been studied up to this time. However, this scheme and the assignments[8] that it is based upon must be viewed with caution until precise ways of calculating CT state energies can be developed.

$$^2S_0 \xrightarrow{h\nu} {}^2S_1(\pi,\pi^*) \tag{1}$$

$$^2S_1(\pi,\pi^*) \rightsquigarrow {}^2T_1(\pi,\pi^*)$$

$$\tau < 2 \text{ ps (unobserved)} \tag{2}$$

$$^2T_1(\pi,\pi^*) \rightsquigarrow [^4T_1(\pi,\pi^*) \rightleftharpoons {}^2T_1(\pi,\pi^*)]$$

$$\tau = 450 \text{ ps (Cu), 2–9 ps (Ag and Mo)} \tag{3}$$

$$[^4T_1(\pi,\pi^*) \rightleftharpoons {}^2T_1(\pi,\pi^*)] \rightsquigarrow {}^2S_0$$

$$\tau = >1 \text{ ns (Cu and Ag), 4 ns (Mo)} \tag{4}$$

In Cu(II) porphyrins the $[^4T_1 \rightleftharpoons {}^2T_1]$ equilibrium of states decays directly to the ground state. In Ag(II) and Mo(V) porphyrins there is good evidence that $^2CT$ states lie below these triplet levels and rapidly relax them to $^2S_0$. In Ag(II) porphyrins these $^2CT$ levels have $(d,\pi^*)$ character,[42] while in Mo(V) porphyrins the lowest energy ones are most likely porphyrin-to-metal charge transfer $[a_{1u}(\pi),a_{2u}(\pi) \rightarrow d_{xy}]$ in character.

On the basis of prior studies which found no emission from OEP complexes of Mo(V)[8] and comparison with $^2S_1$ lifetime estimates ($\tau < 5 \times 10^{-13}$ s) in emissionless Ag porphyrins,[16] we do not expect to observe the ultra-short-lived $^2S_1(\pi,\pi^*)$ state in $OMo(TPP)OCH_3$ ($\tau < 2$ ps; see reaction 2 and Table I). Rather, the 2–9-ps-lived transition seen in Figures 1 and 2 most likely reflects the equilibration of the $^2T_1(\pi,\pi^*)$ and $^4T_1(\pi,\pi^*)$ states (reaction 3). The similarity of the <10 and >100 ps $\Delta A$ spectra is therefore reasonable. The 4-ns-lived transient most likely is due to the decay of the equilibrium distribution of tripquartet and tripdoublet $[^4T_1 \rightleftharpoons {}^2T_1]$ states (reaction 4). Table I notes that this equilibrium of triplet states in Cu(II) porphyrins emits for $\sim$100 $\mu$s at 77 K.[43] However, no such emission is seen from these levels in Ag(II) and Mo(V) porphyrins.[8] Calculations of the electronic level distribution of Ag(II) porphyrins[42] suggest that the singly occupied $d_{x^2-y^2}$ orbital lies below the empty $e_g(\pi^*)$ levels and gives rise to low energy $(d,\pi^*)$ MLCT transitions. Presumably these $^2(d,\pi^*)$

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states are responsible for rapidly relaxing the $[^4T_1 \rightleftharpoons {}^2T_1]$ equilibrium of states and thus make the decay of Ag(II) porphyrins radiationless. Analogously in Mo(V) porphyrins, $^2(\pi,d)$ excited states are likely to lie at lower energy than the $[^4T_1 \rightleftharpoons {}^2T_1]$ manifold of states and thus provide pathways for relaxing them in 4 ns. In both Ag(II) and Mo(V) porphyrins, the spin-allowed relaxation of the low-energy $^2CT$ states to $^2S_0$ is likely to be much faster than their rate of population. Therefore the $^2CT$ states are not likely to be seen.

The possibility that the 4-ns lived transient seen in Figures 1 and 2 is due to recombination of photohomolysis products, $OMo^{IV}(TPP)$ and $\cdot OCH_3$, seems unlikely since this photoreaction has only been found[24] after irradiation into the Soret band at 455 nm, and we are exciting below this band at 527 nm. Also, in THF 75 min of excitation of an aerated solution at 455 nm failed to show any photoreaction. Photohomolysis should have produced a measurable loss of $OMo(TPP)OCH_3$ under these conditions.

**Comparison of $d^1$ and $d^9$ Porphyrins.** Picosecond kinetic and spectroscopic studies of $Cu^{II}(OEP)$, $Cu^{II}(TPP)$, and $Cu^{II}$-(PP-IX-DME) as well as of $Ag^{II}(PP-IX-DME)$ and $Ag^{II}$-(MS-IX-DME) [MS-IX-DME = mesoporphyrin IX dimethyl ester] have been reported previously.[14–16,44] Many of these results are summarized in Table I, which also shows an apparent discrepancy concerning observation of the nanosecond-lived $[^4T_1 \rightleftharpoons {}^2T_1]$ equilibrium of states in Ag(II) porphyrins. Specifically, it has been observed[15] in $Ag^{II}(PP-IX-DME)$ but not in $Ag^{II}(MS-IX-DME)$.[16] Also noted is the fact that the room temperature lifetimes of the $[^4T_1 \rightleftharpoons {}^2T_1]$ manifold have not been well determined for Cu(II) and Ag(II)

porphyrins. Other points of comparison among the $S = {}^1/_2$ metalloporphyrins in Table I concern the lack of observation of the initially populated $^2S_1(\pi,\pi^*)$ level for any of them and the large difference in tripquartet–tripdoublet equilibration rates (reaction 3) between the first-row Cu(II) porphyrin and the second-row Ag(II) and Mo(V) porphyrins. This increased equilibration rate for porphyrins with second-row transition metals could be due to increased spin–orbit coupling effects for these porphyrins relative to ones with first-row transition metals or it could be a consequence of $^2CT$ states mixing with the $[^4T_1 \rightleftharpoons {}^2T_1]$ manifold of states.

The above results on open-shell metalloporphyrins contrast with those of closed-shell systems. In particular the initially formed $S_1(\pi,\pi^*)$ states in Zn(TPP) [with a first-row transition metal like copper] and $Sn(OEP)Cl_2$ [with a second-row transition metal like silver and molybdenum] have lifetimes of 2.7 ns[45] and ~500 ps,[14] respectively. The $d^1$ and $d^9$ open-shell porphyrins have quite different excited-state manifolds and as a consequence show much more rapid relaxation of their initially formed excited states ($\tau < 2$ ps) as well as more complicated decay routes for subsequently formed states.

**Registry No.** OMo(TPP)OCH$_3$, 74751-79-4.

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# Method for Determination of Phosphate Anion–Cation Association Constants from $^{31}P$ Chemical Shifts

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We report an experimental method that utilizes careful measurements of the changes in phosphorus-31 chemical shifts to determine association constants. Chemical shifts of phosphate monoanions and dianions, measured in the presence of cations and referenced to an internal standard, reflect chemical shift changes due to association and can be related quantitatively to the association constants. By this method we have obtained reliable values for dication–phosphate monoanion association constants; even the weak monocation–phosphate monoanion association constants have been measured. For example, the constants for association to dimethyl phosphate monoanion are 3.6 M$^{-1}$ for Mg$^{2+}$ and 0.29 M$^{-1}$ for Na$^+$. Constants have been measured for the association of the dimethyl phosphate anions, the cAMP anion, the ethyl phosphate dianion, and the AMP dianion to Mg$^{2+}$, Ca$^{2+}$, Li$^+$, Na$^+$, K$^+$, and guanidinium ions.

## Introduction

Due to the important biochemical roles of phosphates and polyphosphates and their bound metal ions, the interactions of phosphate anions and cations encompass a set of phenomena that are relevant to many biological processes.[1,2] The association of cations to phosphates in aqueous solution alters phosphate chemical properties, including their reactivity[2] and acidity.[3] It is becoming clear that metal and organic cations

affect nucleic acid structures and, therefore, such nucleic acid functions as transcription and translation.[1] The salient features of the phosphate–cation complex structure with regard to all of these effects are the sites of coordination and the strengths of association of the cations. Cation–phosphate stability constants are therefore essential to a valid interpretation of biological and model studies.[3,4] In this paper, we report a method for the determination of previously unmeasured weak association constants. The method has even given approximate quantitative results for the weak association between mono-

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