



Determination of zero-field splitting parameters for a Mn^{IV} center using variable-temperature, variable-field magnetic circular dichroism spectroscopy: Comparison to electron paramagnetic resonance spectroscopy

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ABSTRACT

The ground and excited state properties of [Mn(OMe)₃(Me₃TACN)]⁺ (Me₃TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane), which features a mononuclear Mn^{IV} center, were investigated using electronic absorption, magnetic circular dichroism (MCD), and variable-temperature, variable-field (VTVH) MCD spectroscopies. Due to small zero-field splittings (ZFSs), Mn^{IV} centers are difficult to study using X-band electron paramagnetic resonance (EPR) spectroscopy. In this work, VTVH MCD spectroscopy was explored as an alternative method. [Mn(OMe)₃(Me₃TACN)]⁺ served as a test complex, because accurate ZFS parameters are available from high-field, high-frequency EPR (HF-EPR) data [33]. Using an *E/D* of 0, as determined from X-band EPR data, the VTVH MCD data collected for [Mn(OMe)₃(Me₃TACN)]⁺ yield an axial ground-state ZFS parameter (*D*) of similar accuracy, but lower precision, than that obtained from HF-EPR spectroscopy (*D* = +0.2(1) and +0.250(5) cm⁻¹ from VTVH MCD and HF-EPR data, respectively). Thus, when combined with X-band EPR spectroscopy, the VTVH MCD method can serve as an alternative to HF-EPR spectroscopy even for systems with small ZFSs. In addition, analysis of electronic absorption and MCD spectral data collected for [Mn(OMe)₃(Me₃TACN)]⁺ permit the extraction of excited state parameters 10*Dq* and *B* (~18490 and 595 cm⁻¹, respectively), which are comparable to those of other Mn^{IV} complexes.

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1. Introduction

High-valent manganese centers participate as key intermediates in a variety of biological and synthetic processes [1–8]. Manganese(IV) centers are also of interest due to their presence in a number of single-molecule magnets [9–11]. With respect to catalytic applications, oxomanganese(V)- and manganese(IV) adducts have been proposed as reactive electrophiles in reactions ranging from water splitting in the oxygen-evolving complex of photosystem II to olefin epoxidation in synthetic manganese-salen complexes [1–6,12–14]. A number of recent reports have emphasized that, in several systems, oxomanganese centers are not the species responsible for substrate oxidation. Instead hydroxo-, hydroperoxo- and iodoarene manganese(IV) adducts serve as active oxidants [15–17]. Given this complex reaction landscape, as well as the short lifetimes of these reactive species, it is important to have

spectroscopic probes that can be used to define the geometric and electronic structures of these intermediates. In addition, there is much current interest in correlating the electronic properties of these high-valent manganese centers with their observed reactivities [8,18–20].

EPR spectroscopy is widely recognized as one of the most powerful tools for examining paramagnetic species [21]. For systems with *S* > ½ ground states, this technique probes both the Zeeman and zero-field splittings of the paramagnetic center, which are described by the spin Hamiltonian in Eq. (1).

$$H = \beta \mathbf{B}gS + D \left[S_z^2 - \frac{1}{3}S(S+1) \right] + E(S_x^2 - S_y^2) \quad (1)$$

The first term is the Zeeman splitting, where β is the Bohr magneton, \mathbf{B} is the magnetic field, g is the Landé g -factor, and S is the spin operator. The final two terms describe the zero-field splitting (ZFS) interaction using the axial (D) and rhombic (E) ZFS parameters. Mononuclear manganese(IV) centers are subject to an axial ZFS that is on the order of microwave frequencies used in conventional X-band experiments (typically 9.4 GHz or 0.3 cm⁻¹). This, along with relatively broad EPR signals, complicates the accurate determination of ZFS parameters from X-band EPR data collected for Mn^{IV} centers. In general, these data are only interpreted to indicate

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whether the D value is large ($\gg 0.3 \text{ cm}^{-1}$) or small ($\ll 0.3 \text{ cm}^{-1}$) compared to the microwave frequency [12,22–32]. For systems with large D values, the rhombicity (E/D) can be identified by the g -value of the low-field transition ($g = 4.1$ and 5.5 for $E/D = 0$ and 0.33). These known shortcomings in X-band EPR studies of Mn^{IV} centers are overcome in high-frequency and high-field (HF) EPR experiments, where the use of larger microwave frequencies (95–700 GHz) [21] permits the determination of D and E from the positions of the EPR resonances [33]. Alternative methods such as inelastic neutron scattering and variable-temperature direct current magnetic susceptibility measurements have been used to determine ZFS parameters for manganese-containing single-molecule magnets [34–36].

Variable-temperature, variable-field magnetic circular dichroism (VTVH MCD) signals of paramagnetic centers can offer an alternative to HF-EPR spectroscopy in the determination of ZFS parameters [37–40]. For mononuclear Co^{II} ($S = 3/2$) and V^{III} ($S = 1$) centers, analysis of VTVH MCD data was shown to provide ZFS parameters essentially identical to those obtained from HF-EPR experiments [41,42]. However, the D values determined by the VTVH MCD method had uncertainties of $\sim 2\text{--}3 \text{ cm}^{-1}$ [41,42]. Thus, the small D values of Mn^{IV} centers, as well as the dependence of the VTVH MCD curves on a total of eight parameters (the transition dipole moment products, M_{xy} , M_{xz} , and M_{yz} , and the ground-state spin Hamiltonian parameters g_x , g_y , g_z , D , and E/D) could hamper the utility of this method.

To evaluate whether VTVH MCD spectroscopy can offer an alternative to EPR spectroscopy in the determination of the ZFS parameters for a mononuclear Mn^{IV} system, we applied this technique to the structurally-defined $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})]^+$ complex ($\text{Me}_3\text{TACN} = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$; see Fig. 1), which was originally reported by Hage and co-workers [43]. This system is an ideal choice as Duboc and Collomb recently obtained highly accurate D and E/D values for this system using HF-EPR spectroscopy ($D = +0.250(5) \text{ cm}^{-1}$ and $E/D = 0$) [33]. We report here that while analysis of VTVH MCD data alone yields ZFS parameters in only modest agreement with those determined by HF-EPR spectroscopy, when the results of X-band EPR and VTVH MCD data are combined, a D value of comparable accuracy, but lower precision, is obtained. In addition, analysis of MCD spectral data allow for the determination of ligand-field parameters $10Dq$ and B .

2. Experimental

2.1. Preparation of $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})](\text{PF}_6)$

All chemicals were obtained from commercial vendors and used without further purification. $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})](\text{PF}_6)$ was obtained following a published synthesis [43]. Several (typically 3–4) recrystallization procedures were performed to obtain brown crystals of $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})](\text{PF}_6)$ that were determined to be pure on the basis electrospray ionization mass spectrometric

data and comparison of electronic absorption extinction coefficients with published values.

2.2. Electronic absorption and MCD spectroscopy

Electronic absorption spectra were collected on a Cary 50 Bio spectrophotometer (Varian). Magnetic circular dichroism data were collected on a spectropolarimeter (Jasco J-815) interfaced with an Oxford Instruments SM-4000-8 magnetocryostat. MCD samples were prepared using solutions of $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})](\text{PF}_6)$ prepared in 9:1 butyronitrile:ethanol, as this solvent system forms a glass upon freezing. Importantly, the room temperature electronic absorption spectra of $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})](\text{PF}_6)$ in acetonitrile and 9:1 butyronitrile:ethanol are identical. VTVH MCD data were obtained from full spectra collected at various magnetic field strengths (0–7 T) and at different temperatures (2–25 K).

2.3. VTVH MCD data analysis

VTVH MCD data were analyzed using a fitting and simulation program developed by Mark J. Riley (University of Queensland) [44,45]. This program employs a formalism developed by Neese and Solomon that has been described in detail elsewhere [37]. Prior to analysis, VTVH MCD datasets were normalized relative to the most intense signal. For all fits, isotropic g -values of 2.00 were assumed, which is reasonable for Mn^{IV} systems, and used in previous simulations of the HF-EPR spectra of $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})](\text{PF}_6)$ [33]. The transition moment products (M_{xz} , M_{yz} , and M_{xy}) and, in certain cases D and E/D (*vide infra*), were adjusted to provide the best fit with the experimental data, as assessed by the χ^2 parameter ($\chi^2 = \sum (f_i^{\text{calc}} - f_i^{\text{exp}})^2$).

2.4. Computations

All computations were performed using the ORCA program (version 2.8.0) [46]. A geometry optimized model of $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})]^+$ was generated with DFT computations using the B3LYP functional [47–49] and TZVP basis set [50,51]. Time-dependent (TD) DFT [52–55] computations were performed within the Tamm-Dancoff approximation using the same functional and basis set. For each calculation, 40 excited states were calculated by including all one-electron excitations within a ± 3 hartree energy window with respect to the highest occupied and lowest unoccupied molecular orbitals (MOs). For comparative purposes, TD-DFT calculations were also performed for $[\text{Mn}^{\text{IV}}\text{Cl}_6]^{2-}$ and $[\text{Mn}^{\text{IV}}\text{F}_6]^{2-}$. Models of these complexes were developed using DFT geometry optimizations with the BP [56,57] functional and TZVP basis set. These calculations were facilitated using the resolution of the identity (RI) approximation [58] that required use of the TZV/J auxiliary basis set. The excited states of these manganese(IV)-halide complexes were also investigated using the multireference SORCI (spectroscopically-oriented configuration interaction) method [59,60]. The SORCI calculations used a CAS(7,7) reference space for both quartet and doublet states, considering seven quartet and eight doublet roots. Calculations performed with a smaller CAS(3,5) active space afforded electronic transitions slightly lower in energy than those obtained using the larger reference space. The inclusion of additional roots did not appreciably affect the transition energies. The threshold parameters T_{sel} , T_{pre} , and T_{nat} were set to 10^{-6} hartrees, 10^{-4} , and 10^{-5} , respectively. Quasi-restricted MOs from a DFT calculation using the BP functional and TZVP basis set provided the starting orbitals for the SORCI calculations.

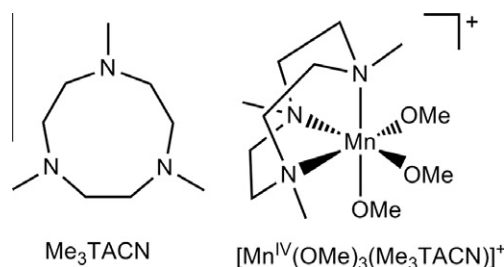


Fig. 1. Schematic structures of Me_3TACN ligand (left) and $[\text{Mn}^{\text{IV}}(\text{OMe})_3(\text{Me}_3\text{TACN})]^+$ complex (1; right).

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