Proceedings of the IV Forum EMR-PL, June 27-29, 2016, Poznań, Poland

EMR Data on Mn(III; S = 2) Ions in MnTPPCl Complex Modelled by Microscopic Spin Hamiltonian Approach

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The electron magnetic resonance data on high-spin (S = 2) manganese(III) $3d^4$ ion in tetraphenylporphyrinato chloride complex (MnTPPCl) obtained by high-frequency techniques are reanalysed. Preliminary results of semiempirical modeling of the spin Hamiltonian parameters for Mn(III) in MnTPPCl are presented. The microscopic spin Hamiltonian approach is utilized to predict the zero-field splitting and the Zeeman electronic parameters. It is found that for Mn(III) ions in MnTPPCl matching the experimental spin Hamiltonian parameters and the theoretical ones based on the ligand-field energy levels (Δ_i) within the 5D multiplet only may not be suitable for this system. Contributions due to the levels arising from the higher-lying 3H multiplet need to be taken into account in order to determine the reasonable values of microscopic parameters describing Mn(III) ions in MnTPPCl.

DOI: 10.12693/APhysPolA.132.15

PACS/topics: 33.35.+r, 71.70.Ch, 71.70.Ej, 76.20.+q, 76.30.-v, 76.30.Fc, 87.80.Lg

1. Introduction

The transition metal complexes play an important role in chemistry and biology due to their electronic structure. Since the incompletely filled 3d shell leads to paramagnetism, the best method to investigate their magnetic and spectroscopic properties is electron magnetic resonance (EMR, which includes also EPR/ESR) [1–3] based on the effective spin Hamiltonian (SH) [4, 5]. Due to the large zero-field splitting (ZFS) characteristic for integer spin $3d^4$ and $3d^6$ systems, see e.g. [6, 7], the high-field EMR and high-frequency (HMF-EMR) techniques are best suited for detection of the allowed spin transitions [8–10]. Early studies of SH parameters of Mn(III) ions in porphyrinic and related complexes have been reviewed in [11], whereas more recent studies include, e.g. [12–14].

Using HMF-EMR Krzystek et al. [11] have obtained complete powder spectra of the high-spin (S = 2) manganese(III) $3d^4$ ion in 5,10,15,20-tetraphenyl-21H,23Hporphine chloride complex (MnTPPCl), which exhibits axial symmetry, and elucidated its electronic structure. The axial ZFS parameter (ZFSP) was determined as $D = b_2^0 = -2.31 \text{ cm}^{-1}$ and the g-factor as close to 2.00 [11]. Attempts to rationalize these results in terms of the microscopic spin Hamiltonians (MSH) approach have also been made, however, the contributions due to the electronic spin-spin (SS) coupling (SSC) and the fourthrank ZFSPs, admissible for spin S = 2, have not been taken into account therein [11]. In this paper we present preliminary results of semiempirical modeling of the SH parameters for Mn(III) ions in tetraphenylporphyrinato chloride complexes utilizing the MSH approach developed up to fourth-order perturbation theory [6, 15] for $3d^4$ and $3d^6$ systems with S = 2 within the ground 5D multiplet. Calculations of the ZFSPb₂⁰ (= D) and the Zeeman electronic (Ze) factors g_i are carried out for wide ranges of values of the microscopic parameters using the MSH/VBA package [6]. The aim of this study is to elucidate the intrinsic magnetic nature of Mn(III) ions at tetragonal symmetry sites and verify suitability of the studied crystals for application as high-pressure probes for HMF-EMR [8–10] studies.

2. Theoretical background

The theoretical background for this study is provided by the physical Hamiltonians, including the crystal (ligand) field (CF) terms [16–19], and the effective spin Hamiltonians (SH), including the ZFS and Ze terms [1– 5]. The underlying theory has been outlined in the full paper together with pertinent references [20]. Here we only recap the key points and defined the notations used. The *physical* zero-field splitting (ZFS) within the states of an orbital singlet ground state $|\Gamma_0\rangle |S=2, M_s\rangle$ is due to the combined action of the spin-orbit coupling (SOC) and the electronic spin–spin (SS) coupling acting within the CF states. In the MSH approach only the states arising from the ground ⁵D (S = 2) multiplet are considered [6, 7, 15]. Using the complete matrix diagonalization incorporated into the crystal field analysis (CFA) package [21] and its extension CFA/MSH package [22] all states within the whole $3d^4$ and $3d^6$ configuration are taken into account. The role of the contributions to the ZFS parameters (ZFSP) for Fe^{2+} in several systems arising from the higher lying spin-triplet ${}^{3}L$ (S = 1) states was studied in [23, 24]. It appears that these contributions may be important, as compared with the 5D approximation. Krzystek et al. [11] used a mixed approach.

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i.e. in addition to the second-order perturbation theory terms within the 5D approximation, the ZFSP contributions due to one state of the higher spin-triplet 3H was taken into account. A question of compatibility of the respective results is considered in this study.

The general form of the Ze and ZFS terms in SH expressed in terms of the extended Stevens operators (ESO), O_k^q , defined in [25, 26] is written as

$$H = H_{Ze} + H_{ZFS} = \mu_{\rm B} \boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S}$$

+
$$\sum_{k=2,4,6} \sum_{q=-k}^{k} B_{k}^{q} O_{k}^{q} \left(S_{x}, S_{y}, S_{z} \right) = \mu_{\rm B} \boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S}$$

+
$$\sum_{k=2,4,6} \sum_{q=-k}^{k} f_{k} b_{k}^{q} O_{k}^{q} \left(S_{x}, S_{y}, S_{z} \right).$$
(1)

Equation (1) is suitable for transition ions at triclinic symmetry sites, whereas for tetragonal symmetry the second-rank ZFS terms in the conventional notation [4, 5] used in [11] are

$$H_{ZFS} = B_2^0 O_2^0 = \frac{b_2^0 O_2^0}{3} = D \left[S_z^2 - \frac{S(S+1)}{3} \right].$$
(2)

The conversion relation applies $D = 3B_2^0 = b_2^0$. In the case of the negative axial ZFSP $b_2^0 < 0$, which will be discussed in here, the ground *effective* spin state is $|2, \pm 2\rangle$, whereas for $b_2^0 > 0$ the state $|2, 0\rangle$. The modelling of the ZFSPs and the *g*-factors, measured by HMF-EMR [11], are carried out for Mn(III) ions in MnTPPCl using the MSH/VBA package [6].

3. Electronic structure of Mn(III) ions in MnTPPCl

The available crystallographic, magnetic, and spectroscopic data on Mn(III) ions in MnTPPCl have been summarized in [20]. Mn(III) ions occupy the distorted octahedral sites with tetragonal C_{4v} symmetry. The expected energy levels and the respective wave functions in Cartesian coordinates expected for Mn(III) ions at octahedral and tetragonal sites [27] are depicted in Fig. 1. The energy relations in terms of the conventional [17, 19] CF parameters (CFPs) provided in [11] are also indicated. Assignment of the wave functions corresponding to the energy levels in Fig. 1 is adapted from [11] as follows: ${}^{5}B_{1g} = d_{x^2-y^2}$, ${}^{5}A_{1g} = d_{z}^2$, ${}^{5}E_{g} = (d_{xz}, d_{yz})$, ${}^{5}B_{2g} = d_{xy}$, whereas the energy spacing were originally [11] denoted as: $\delta_1 = {}^{5}E_g \rightarrow {}^{5}B_{2g}, \delta_2 = {}^{5}B_{1g} \rightarrow {}^{5}A_{1g}, \delta_3 = {}^{5}B_{1g} \rightarrow {}^{3}E$, and $\Delta = {}^{5}B_{1g} \rightarrow {}^{5}B_{2g}$. The equivalence of δ_i and Δ with the energy spacing Δ_i used in the MSH/VBA package [6] is given by: $\Delta_1 = \Delta_2 \approx \Delta - \delta_1$, $\Delta_3 \approx \Delta$, $\Delta_4 \approx \delta_2$.

The sequence of energy levels (ELs) adopted in [11], based on the literature values of the conventional CFPs, and correspondence between the wave functions in Fig. 1 and those in the notation $|L, \pm M_L\rangle$ defined in the MSH/VBA package [6, 15] is provided in [20]. Guided by the predictions of the ELs [11], an initial set of input (i.e. microscopic) parameters for our calculations is selected as (in cm⁻¹): $\Delta_1 = \Delta_2 = 22500$, $\Delta_3 = 25000$,



Fig. 1. Schematic energy levels (not in scale) arising from the free ion (FI) ${}^{5}D$ (d^{4}) term for Mn(III) ions at octahedral (OH) and axially elongated tetragonal (TE) complexes exhibiting negative ZFSP *D*. For axially compressed tetragonal complexes positive ZFSP *D* is expected [27] resulting in inversion of spin levels.

 $\Delta_4 = 21500$, the SOC constant λ in the range 50 to 110, and the SSC constant $\rho = 0.18$ [28]. Additionally, for tetragonal symmetry the mixing coefficients [6, 15] satisfy the relations: q = 1, s = 0. Note that the SOC constant λ in crystal is reduced from the free ion value $\lambda_0 : \lambda = k \times \lambda_0, k \leq 1$, due to the orbital (covalency) reduction [16, 17, 19]. The values λ_0 available in literature range from: 83.4 cm⁻¹ [29], 88 cm⁻¹ [6, 30, 31], 89 cm⁻¹ [32], 90.4 cm⁻¹ [16], to 110 cm⁻¹ [28].

To take into account the contributions to the ZFSPs and g-factors arising from the higher-lying ${}^{3}H$ multiplet states (see Fig. 1) the relation [11]:

$$D' = -\frac{\xi^2}{4\Delta E \left({}^3E - {}^5A_1\right)} \tag{3}$$

for ${}^{5}B_{1}$ ground state, where $\xi = 2S\lambda = 4\lambda$, is utilized. Note that for the cases of $3d^{4}$ (e.g. Cr^{2+}) and $3d^{6}$ (e.g. Fe^{2+}) ions, where the spin-triplet states are much higher in energy than the spin-quintet states [33], the ${}^{5}D$ approximation can be considered sufficiently reliable. However, the study [11] indicates that this condition may not be well satisfied for the case of Mn(III) ion at tetragonal C_{4v} symmetry sites in MnTPPC1.

4. MSH modelling of the ZFS parameters for Mn(III) ions in MnTPPCl

The energy levels for Mn(III) ion at tetragonal symmetry sites in MnTPPCl (see Fig. 1) correspond to the energy level scheme denoted as "case 2" in the MSH/VBA program [6, 15], which is utilized for MSH modelling of the ZFSPs and the *g*-tensor components for Mn(III) ions in MnTPPCl.Calculations carried out using the initial set of input parameters (see above) yielded the variation of the total ZFSPs versus λ depicted in Fig. 2, whereas the specific contributions of the ZFSPs are listed in Table I. Since the experimental values were determined [11]

The contributions to the ZFSPs (in cm⁻¹) calculated for the input parameter values as listed in text ($\lambda = 80 \text{ cm}^{-1}$).

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$b_2^0(ho)$	-0.54	$b_4^0(\lambda^4)$	7.46×10^{-5}
$b_2^0(\lambda^2)$	-0.74	$b_{4}^{0}(ho^{2})$	1.8×10^{-5}
$b_2^0(\lambda^3)$	-0.006	$b_4^0(ho\cdot\lambda^2)$	$7.79 imes 10^{-5}$
$b_2^0(\lambda^4)$	1.88×10^{-4}	total b_4^0	1.7×10^{-4}
$b_2^0(ho^2)$	1.65×10^{-6}	$b_4^4(\lambda^4)$	-3.39×10^{-4}
$b_2^0(ho\cdot\lambda)$	-0.0058	$b_{4}^{4}(\rho^{2})$	-1.36×10^{-4}
total b_2^0	-1.29	$b_4^4(ho\cdot\lambda^2)$	-6.3×10^{-4}
		total b_4^4	-0.0011

TABLE II

The contributions to the g-tensor components g_{\parallel} and g_{\perp} (dimensionless) calculated for the input parameter values as listed in text; g_e denotes the free-ion value 2.0023 ($\lambda = 80 \text{ cm}^{-1}$).

g_i	$g_e + g_i(\lambda)$	$g_i(\lambda^2)$	$g_i(g_e\lambda^2)$	Total
$g_x = g_y = g_\perp$	1.9952	1.3×10^{-5}	-27×10^{-5}	1.995
$g_z = g_{\parallel}$	1.9767	-5.8×10^{-5}	$ -27 \times 10^{-5} $	1.976

as $g_{\parallel} = 1.98(2)$ and $g_{\perp} = 2.005(3)$, we have rounded the theoretical values in Table II accordingly. Full analysis will be given in [20].

5. Discussion

Analysis of the MSH modelling results in Tables I and II, which illustrate the role of various contributions enabling the following comments. It appears that for Mn(III) ions at tetragonal symmetry sites the dominant contributions to b_2^0 arise from $b_2^0(\lambda^2)$ and $b_2^0(\rho)$, whereas to g_i from $g_i(\lambda)$. Unlike for Fe(II) ions the contributions arising from the higher-order perturbation theory play insignificant role. This is due to the different sequence and magnitude of the energy levels [6, 7].

A survey of selected data available for Mn(III) ions in porphyrinic and related complexes [20] yields the values of b_2^0 (= D) in the range $-1.5 \text{ cm}^{-1} < b_2^0 < -3 \text{ cm}^{-1}$. Hence, Fig. 2 and Table I reveal that agreement with the experimental b_2^0 (= D) values may be achieved for some complexes, however, it is not the case of MnTPPCl [11]. It appears that the ZFSPs estimated based on the ligandfield energy levels (Δ_i) within the ⁵D multiplet only may not be suitable for this system. To match tentatively the experimental SH parameters and the theoretical ones for Mn(III) ions in MnTPPCl we take into account the specific contribution D' [11], which is due to some levels arising from the higher-lying ${}^{3}H$ multiplet. The values of the total b_2^0 (= D) calculated including the contribution D' (see Fig. 2) show that an agreement is achievable for a reasonable values of λ (in crystal) around 80 cm⁻¹ or less if the energy difference $\Delta E ({}^{3}E - {}^{5}A_{1})$ would decrease. Detailed results of the semiempirical modeling of the SH parameters aimed at elucidation of the intrinsic magnetic nature of Mn(III) ions at tetragonal symmetry sites in MnTPPCl and related systems as well as full analysis will be provided in [20]. The question of suitability of the studied crystals for application as highpressure probes for HMF-EMR [8-10] studies will be also discussed therein.



Fig. 2. Variation of the ZFSPs (in cm⁻¹) versus λ for the input parameters defined in text: (a) all ZFSPs, (b) fourthrank ZFSPs magnified from part (a). Experimental value b_2^0 (= D) ≈ -2.31 cm⁻¹ for Mn(III) in MnTPPCl [11] is indicated by a straight line. The magenta line (open triangles) represents the values of b_2^0 (= D) calculated including the contribution D' (see text).

Here we only mention recent extensive experimental and theoretical studies [34] of peroxomanganese(III) complex supported by a scorpionate ligand, which exhibits orthorhombic site symmetry. The authors [34] used electronic absorption, EMR, low-temperature magnetic circular dichroism (MCD), and variable-temperature variable-field (VTVH) MCD spectroscopies. Theoretical calculations [34] employed several density functional theory (DFT) methods, namely, time dependent (TD- DFT), coupled-perturbed (CP-DFT) DFT, and multireference *ab initio* CASSCF/NEVPT2. Detailed discussion of the results [34] will be provided in [20]. Here we mention only that the CP-DFT computations have revealed that the dominant contribution to D was through spin–orbit coupling ($D_{SOC} = -1.37 \text{ cm}^{-1}$), whereas the spin–spin coupling contribution was found non-negligible ($D_{SS} = -0.32 \text{ cm}^{-1}$). However, the value of D_{SOC} was slightly underestimated relative to the experimental $D = -2.0 \text{ cm}^{-1}$. Interestingly, the stateaveraged CASSCF/NEVPT2 method predicted overestimated value: $D_{SOC} = -2.91 \text{ cm}^{-1}$.

Hence, a caution is needed when assessing the DFT results as well as an overall importance of the higher-lying spin-triplet states. Note that other states not included in D' may also contribute to the total D, whereas various contributions may cancel each other [23, 24, 34]. The study [34] indicates also that the SSC constant $\rho = 0.18 \text{ cm}^{-1}$ adopted by us yields proportionally larger values of the ratio $D_{SS}/D_{SOC} = 0.73$ than that predicted in [34] for peroxomanganese(III) complex $D_{SS}/D_{SOC} =$ 0.23. To clarify the role of the SS contributions $b_2^0(\rho)$ more reliable values of the SSC constant is needed. In view of the site symmetry lower than axial in peroxomanganese(III) complex [34] these preliminary conclusions on applicability of DFT-based methods might not be fully justified. In order to make a more accurate assessment, calculations using the CFA or CFA/MSH package [21, 22] within the whole $3d^4$ configuration and incorporating lower symmetry would be indispensable, which are beyond the scope of this paper. Once new theoretical results become available, the present predictions may be verified and fine-tuned, yielding more reliable ranges of the microscopic parameter values feasible for Mn(III) ions in MnTPPCl and other structurally related systems. This work is in progress.

Acknowledgments

This work was partially supported by the research grants from the Polish National Science Center: DEC-2012/04/M/ST3/00817 (Cz.R.) and UMO-2014/15/B/ST4/04946 (K.T.).

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