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John D. Harvey, Christopher J. Ziegler, Joshua Telser, Andrew Ozarowski, and J. Krzystek*: High-Frequency and -Field EPR Investigation of a Manganese(III) N-Confused Porphyrin Complex, [Mn(NCTPP)(py)$_2$]

Pages 4451−4453. In our original paper,[1] we used ligand-field parameters [as defined by Ballhausen[2] and estimated earlier[3] for Mn(III) porphyrins (values in cm^{-1}): $Dq = 2700$, $Ds = 2800$, $Dt = 2400$] as a starting point for analyzing zero-field splitting (zfs) in [Mn(NCTPP)(py)$_2$]. These parameters were modified to account for the increased equatorial field expected from the N-confused porphyrin ligand. This effect was achieved by reducing the magnitude of the tetragonal parameter, Dt (from 2400 to 1800 cm^{-1}), which indeed increases the magnitude of the axial zfs, D. The calculation is correct, but the rationale is wrong. Such a *reduction* in the magnitude of Dt corresponds to a stronger axial field, which is functionally equivalent to a *weaker* equatorial field (i.e., reduction of Dt to zero would correspond to equal axial and equatorial field strengths). Therefore, Dt should have been increased, but this reduces the magnitude of D, as shown by perturbation theory equations described previously.[3] The larger magnitude of D observed for [Mn(NCTPP)(py)$_2$] relative to that in typical Mn(III) tetrapyrroles instead can be modeled simply by decreasing the Racah parameters[4] from the value used for porphyrins. Values for $B = 800$, 700, and 600 cm^{-1} respectively yield $D = -2.38$, -2.68, and -3.07 cm^{-1}. The first of these D values is typical for Mn(III) porphyrins; the last corresponds to that observed for [Mn(NCTPP)(py)$_2$]. These lower values of the Racah parameters qualitatively reflect increased covalency of the NCTPP macrocycle relative to standard tetrapyrroles.

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(1) Harvey, J. D.; Ziegler, C. J.; Telser, J.; Ozarowski, A.; Krzystek, J. *Inorg. Chem.* **2005**, *44*, 4451−4453.

(2) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962.

(3) Krzystek, J.; Telser, J.; Pardi, L. A.; Goldberg, D. P.; Hoffman, B. M.; Brunel, L.-C. *Inorg. Chem.* **1999**, *38*, 6121−6129.

(4) Only B is varied independently; $C \equiv 4.3B$.