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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 Ballhausen² and estimated earlier³ 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 parameters⁴ 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; $C \equiv 4.3B$.