

Synthesis of Imidazolate Bridged Di- and Tri-nuclear Ferromagnetic Complexes of Chromium(III) Porphyrins

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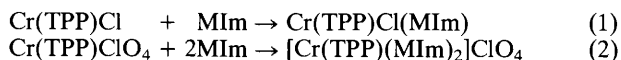
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Reaction of a metal imidazolate complex, MIm (M=Cu^{II} or Ni^{II}), with Cr(TPP)Cl or Cr(TPP)ClO₄ affords the dinuclear complexes, Cr(TPP)(MIm)Cl, and the trinuclear complexes, [Cr(TPP)(MIm)₂]ClO₄ (TPP is the dianion of tetraphenylporphyrin), respectively, which exhibit ferromagnetic coupling in the Cr–Cu complexes.

There has been considerable activity recently in the prediction of magnetic coupling interactions in dinuclear complexes based on symmetry considerations of the magnetic orbitals. Ferromagnetic coupling is predicted when the magnetic orbitals are orthogonal and antiferromagnetic coupling results when the orbitals are non-orthogonal.¹ Such predictions can be made from the single crystal X-ray structure and in some instances from a knowledge of the probable orientation of magnetic orbitals in the complex, and in general have proven highly useful in a wide array of heterodinuclear systems.² For example chromium(III) dinuclear complexes with octahedral nickel(II) were predicted to be ferromagnetic as early as 1971³ on the basis that the chromium's (t_{2g})³ electron configuration and the nickel's (e_g)² configuration were orthogonal. This prediction was verified recently in a Cr^{III}–Ni^{II} tetranuclear complex for which magnetic data has been published.⁴

We herein report the synthesis of two dinuclear and two trinuclear imidazolate bridged heteronuclear complexes of chromium(III) porphyrins, which can be used to verify the previously mentioned predictions. Our interest in this area also stems from the recent reports describing ferromagnetic interactions in Cr^{III}–S–Cr^{III},⁵ Cr^{III}–O–Cr^{III},⁶ Cr^{III}–OH–Cr^{III},⁷ Cr^{III}–O–Ni^{II},⁴ and Cr^{III}–O–Cu^{II}⁸ systems and antiferromagnetic behaviour in others, Cr^{III}–O–Fe^{III}⁹ and Cr^{III}–O–Cr^{III}¹⁰ and our own investigations into imidazolate bridged heteronuclear complexes of metalloporphyrins.¹¹

The synthesis of the di- and tri-nuclear complexes is easily accomplished by the reaction of a metal imidazolate complex, MIm,¹² (see Figure 1) with Cr(TPP)Cl (TPP is the dianion of tetraphenylporphyrin) (1:1 molar ratio) and Cr(TPP)ClO₄ (2.5:1 molar ratio), respectively, in acetone/toluene and toluene at reflux for 1 h [equations (1) and (2)]. On cooling, the products precipitated, were removed by filtration, and were recrystallized from toluene.



A single set of isobestic points is observed at 383, 398, 408, 451, 481, 577, 592, 607, and 640 nm in the titration of Cr(TPP)Cl with the MIm complexes [equation (3)]. Plots of $\ln[A - A_0/A_c - A]$ [A_0 is the absorbance of Cr(TPP)Cl, A_c is the absorbance of Cr(TPP)Cl(MIm), and A is the absorbance

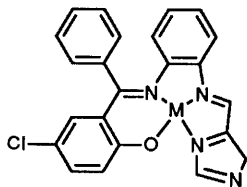
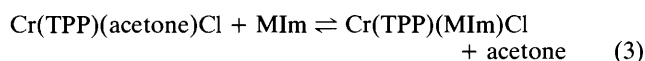


Figure 1. Structure of metal imidazolate complex, MIm. M = Cu^{II} or Ni^{II}.

of an equilibrium mixture] vs. $\ln[\text{MIm}]_{\text{eq}}$ for the reaction of Cr(TPP)Cl with CuIm and NiIm in toluene/acetone (80%/20%) at 35°C gave slopes of 0.94 and 1.00, consistent with the formation of a 1:1 adduct, and formation constants of 5.67×10^5 and 9.22×10^5 , respectively. The values observed here are consistent with the formation constant of 6.3×10^5 at 25°C which was observed in the reaction of Cr(TPP)Cl with 1-methylimidazole.¹³



Titration of Cr(TPP)ClO₄ with MIm indicates that the addition of this ligand is stepwise as was the case for pyridine (pyr).¹³ However, the isolated product under the synthetic conditions is the bisadduct as shown by the spectroscopic and magnetic data given below. The major visible spectral difference between the dinuclear complexes (monoadducts), Cr(TPP)(MIm)Cl (401, 453, 576, and 613 nm), and trinuclear complexes (bisadducts), [Cr(TPP)(MIm)₂]ClO₄, (404, 457, 571, and 608 nm), is in the positions of bands III and IV as was the case for the Cr(TPP)Cl(pyr), [Cr(TPP)(pyr)₂]ClO₄ pair. The monoadducts exhibit bands at 576 and 613 nm while the bisadducts exhibit bands at 571 and 608 nm. Further evidence that the adducts of Cr(TPP)ClO₄ with MIm are trinuclear is afforded by the IR frequencies of the perchlorate. The Cr(TPP)ClO₄, which contains a bound perchlorate, exhibits bands at 1122 and 627 cm⁻¹ and its adducts with MIm, at 1106 and 624 cm⁻¹. The shifts of these bands and the sharpening of the 1106 cm⁻¹ band indicate that the perchlorate in the adducts is unco-ordinated,¹⁴ which supports their formulation as trinuclear complexes.

The adducts of metalloporphyrins with MIm afford interesting compounds to probe the orbital basis of magnetic coupling interactions. The nickel complexes, Cr(TPP)Cl–NiIm and [Cr(TPP)(NiIm)₂]ClO₄, serve as noncoupled blanks of the copper complexes, Cr(TPP)Cl–CuIm and [Cr(TPP)(CuIm)₂]

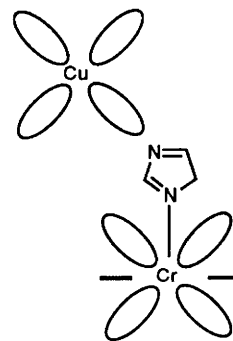


Figure 2. Orbital basis of ferromagnetism in the Cu^{II}–Cr^{III} adducts. The copper's unpaired electron is in its d_{x²-y²} orbital which overlaps with the bridging imidazolate. The chromium's three unpaired electrons are in its t_{2g} set. Only one of the chromium's t_{2g} orbitals is shown.

ClO_4 , since the square planar nickel complex is diamagnetic and thus not capable of magnetic coupling. The adducts of NiIm with $\text{Cr}(\text{TPP})\text{Cl}$ and $\text{Cr}(\text{TPP})\text{ClO}_4$, $\text{Cr}(\text{TPP})(\text{NiIm})\text{Cl}$ and $[\text{Cr}(\text{TPP})(\text{NiIm})_2]\text{ClO}_4$, gave magnetic moments of 4.06 and 4.14 μ_{B} , respectively, which are close to the spin only value of 3.89 μ_{B} for a d^3 electron configuration. Ferromagnetism is predicted for the adducts of Cr^{III} and low spin Fe^{III} with Cu^{II} since the magnetic orbitals of these metal atoms (t_{2g})³ and (t_{2g})⁵, respectively, are orthogonal to the copper's $d_{x^2-y^2}$ magnetic orbital as shown in Figure 2. Recent work with $[\text{Fe}(\text{TPP})(\text{CuIm})_2]\text{B}_{11}\text{CH}_{12}$, which should be isostructural to the $[\text{Cr}(\text{TPP})(\text{CuIm})_2]\text{ClO}_4$ complex, provided the first example of ferromagnetic coupling through an imidazolate bridge with $J = 22 \text{ cm}^{-1}$.¹⁵ The magnetic moments of the adducts of CuIm with $\text{Cr}(\text{TPP})\text{Cl}$ and $\text{Cr}(\text{TPP})\text{ClO}_4$ are 4.42 and 5.99 μ_{B} , respectively. These can be compared to the noncoupled values of 4.24 and 4.58 μ_{B} and the ferromagnetic limiting values of 4.89 and 5.92 μ_{B} . The noncoupled values are given by $u = [\sum g^2 S_i(S_i + 1)]^{1/2}$ with $g = 2$ and S_i being the spin state of each metal. The ferromagnetic limiting values are calculated as $u = g[S_{\text{T}}(S_{\text{T}} + 1)]^{1/2}$ where $g = 2$ and $S_{\text{T}} = 2$ for $\text{Cr}(\text{TPP})(\text{CuIm})\text{Cl}$ and 5/2 for $[\text{Cr}(\text{TPP})(\text{CuIm})_2]\text{ClO}_4$.

Further work on the characterization of the ferromagnetic chromium(III) and iron(III) low spin complexes and the contrasting antiferromagnetically coupled $\text{Mn}(\text{TPP})\text{-Cu}^{\text{II}}$ ¹⁶ and $\text{M}^{\text{III}}\text{-Cu}^{\text{II}}$ ($\text{M}=\text{Fe}$ or Mn)¹⁷ compounds will aid our understanding of magnetic exchange interactions in general and the ability of the imidazolate bridge to foster both ferromagnetic and antiferromagnetic coupling in particular.

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References

- 1 C. J. Cairns and D. J. Busch, *Coord. Chem. Rev.*, 1986, **69**, 1.
- 2 A. Bencini, C. Benelli, A. Dei, and D. Gatteschi, *Inorg. Chem.*, 1985, **24**, 695; M. Julve, M. Verdaguer, M. F. Charlot, O. Kahn, and R. Claude, *Inorg. Chim. Acta*, 1984, **82**, 5; O. Kahn, J. Galy, Y. Journaux, J. Jaud, and I. Morgenstern-Badarau, *J. Am. Chem. Soc.*, 1982, **104**, 2165.
- 3 A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45.
- 4 Y. Pei, Y. Journaux, and O. Kahn, *Inorg. Chem.*, 1989, **28**, 100.
- 5 A. A. Pasynskii, I. L. Eremenko, G. S. Gasanov, O. G. Ellert, V. M. Novotortsev, Y. V. Rakin, T. K. Kurbanov, and V. Kalinnikov, *Polyhedron*, 1984, **3**, 775.
- 6 C. Reber, H. U. Guedel, L. Spiccia, and W. Marty, *Inorg. Chem.*, 1987, **26**, 3186.
- 7 E. E. Eduok, J. W. Owens, and C. J. O'Connor, *Polymer*, 1984, **3**, 17.
- 8 Y. Journaux, O. Kahn, J. Zarembowitch, J. Galy, and J. Jaud, *J. Am. Chem. Soc.*, 1983, **105**, 7985.
- 9 R. L. Elliott, P. J. Nichols, and B. O. West, *Aust. J. Chem.*, 1986, **39**, 975.
- 10 D. J. Liston and B. O. West, *Inorg. Chem.*, 1985, **24**, 1568.
- 11 C. T. Brewer and G. A. Brewer, *Inorg. Chem.*, 1987, **26**, 3420; C. T. Brewer and G. A. Brewer, *J. Inorg. Biochem.*, 1986, **26**, 247; C. T. Brewer and G. A. Brewer, *Inorg. Chim. Acta*, 1986, **111**, L5.
- 12 R. Atkins, G. A. Brewer, E. Kokot, G. M. Mockler, and E. Sinn, *Inorg. Chem.*, 1985, **24**, 127.
- 13 F. Basolo, R. D. Jones, and D. A. Summerville, *Acta Chem. Scand.*, 1978, **32**, 771.
- 14 C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kastner, W. R. Scheidt, K. Spartalian, and G. Lang, *J. Am. Chem. Soc.*, 1979, **101**, 2948.
- 15 C. A. Koch, C. A. Reed, G. A. Brewer, N. P. Rath, W. R. Scheidt, G. Gupta, and G. Lang, *J. Am. Chem. Soc.*, 1989, **111**, 7645.
- 16 C. A. Koch, B. Wang, G. Brewer, and C. A. Reed, *J. Chem. Soc., Chem. Commun.*, 1989, 1754.
- 17 N. Matsumoto, Y. Maeda, H. Okawa, T. Akui, T. Kawaji, A. Ohyoshi, M. Kadera, H. Oshio, and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1989, 943.