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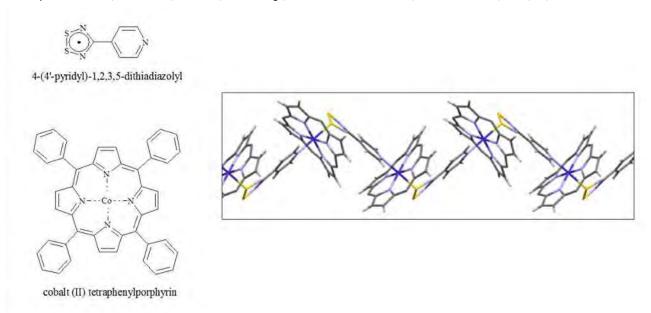
Coordination of a neutral thiazyl radical to Co(II) tetraphenylporphyrin

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The 1,2,3,5-dithiadiazolyl radicals (R-CNSSN) are of considerable interest due to their potential as building blocks for materials with interesting magnetic or conducting properties. The behaviour of these neutral radicals as ligands has also been investigated [1]. Reactions with Pt(0) and Pd(0) have been shown to yield complexes where coordination to the metal is through sulfur, and the S-S bond in the radical is broken [2]. More recent work has shown that coordination through the radical nitrogen is possible with 2'-pyridyl-substituted dithiadiazolyl in combination with strongly electron-withdrawing ligands. Several of these complexes show magnetic coupling between the radical and the metal centre [3]. We have recently begun investigating the coordination of dithiadiazolyls to metalloporphyrins. The crystal structure of a coordination polymer formed between 4-(4'-pyridyl)-1,2,3,5-dithiadiazolyl and cobalt(II) tetraphenylporphyrin has been determined. The radical in this complex is coordinated through one sulfur atom, a coordination mode for dithiadiazolyls that has not previously been observed. Formation of the complex in solution has been investigated using EPR and UV-vis. Irradiation of a solution of the diamagnetic complex with intense white light leads to homolysis of the radical-ligand bond, observed by EPR. Our investigations of complex formation involving other dithiadiazolyl derivatives with a series of metalloporphyrins will also be presented.

[1] K. E. Preuss, Dalton Trans., 2007, 2357-2369., [2] A. J. Banister, I. May, J. M. Rawson and J. N. B. Smith, J. Organomet. Chem., 1998, 550, 241-243., [3] see for example E. M. Fatila, J. Goodreid, R. Clérac, M. Jennings, J. Assoud and K. E. Preuss, Chem. Commun., 2010, 46, 6569-6571.



Keywords: thiazyl radicals, coordination polymer