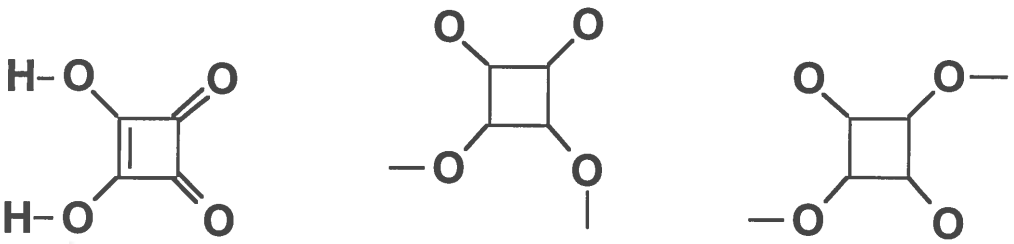
Metal Squarates: Structural Factors Affecting Physical Properties

Adeana Bishop Literature Seminar November 16, 1995

Paramagnetic metal centers bridged by squarate ligands have become a subject of interest because of their relations to well classified oxalate [1] and 2,2'-bipyrimidine [2] bridged complexes which exhibit strong magnetic coupling. The squaric acid dianion, the dianion of 3,4-dihydroxycyclobutenedione (Figure 1), is a rational choice for producing materials which display magnetic exchange because of its unique electronic properties [3] and its ability to coordinate in a variety of modes [4]. Copper centers bridged by the squarate ligand can demonstrate antiferromagnetic coupling at distances up to 7.8 Å [5]. However, intrametallic distance is only one consideration in the magnitude of antiferromagnetic exchange [6]. An overview of squarate ligands which bridge iron [1,7], lanthanide [8,9], vanadium [10], copper [5,11,12,13,14,15], and heterometallic [16,17] centers will elucidate the primary factors affecting the magnetic exchange.



squaric acid μ-1,2 mode μ-1,3 mode

Figure 1.

A significant factor affecting the magnetic exchange between the metal centers through the bridging squarate anion is the orbital overlap between the highest occupied molecular orbital of the metal and the molecular orbitals of the squarate anion. That is, the unpaired electron of the metal must occupy an orbital which has the correct symmetry to allow mixing with the orbitals of the squarate. This factor has yet to be controlled through rational synthesis, and as a result, many of the metal squarates have very weak magnetic coupling.

The second parameter related to the magnitude of antiferromagnetic exchange in metal squarate systems is the squarate ligand coordination mode. The anion can coordinate as a monodentate, bidentate, tetradentate, and bis-chelating ligand [18]. Two metals can coordinate to the squarate anion in either a μ-1,2 or μ-1,3 coordination mode (Figure 1). In general complexes coordinated in the μ-1,2 mode have larger values of magnetic exchange than those coordinated in the μ-1,3 mode. Tetradentate and bis-chelating coordination modes, while less common, offer promise for better exchange interactions.

The third consideration is the amount of π electron delocalization on the squarate complex [19]. The amount of delocalization on the squarate ligand can be compared by the difference in the longest C-C bond and the shortest C-C bond in the squarate, Δ(C-C), and the difference in the longest C-O bond and the shortest C-O bond, Δ(C-O) [15]. Small values of Δ(C-C) and Δ(C-O) correspond to significant delocalization of double bond character over the squarate ring, resulting in stabilization of the spin states on the metal and diminution of the antiferromagnetic exchange.

To achieve strong magnetic exchange for complexes containing metal centers bridged by squarate anions, all of these parameters must be considered. To date, this has not been accomplished. Consequently, the magnetic properties of metal squarates have only been slightly improved. Comparing the most promising example of a copper tetrakis system (Figure 2) to early binuclear systems, the values of the exchange parameters have increased tenfold, but these values are still an order of magnitude lower than those for similar oxocarbon bridged systems.

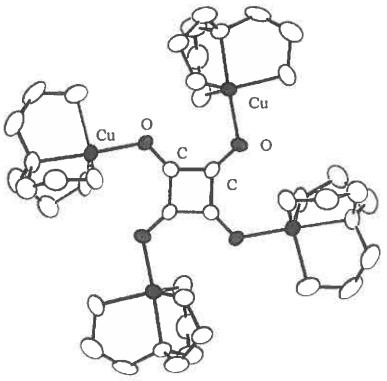


Figure 2.

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