This Week's Citation Classic

Kato M, Jonassen H B, Fanning J C & Cusachs L C. Copper(II) complexes with subnormal magnetic moments. *Chem. Rev.* **64**:99-128, 1964.
[Richardson Chemistry Lab., Tulane Univ., New Orleans, LA]

This paper reviewed the papers for copper(II) complexes with subnormal magnetic moments up to the middle of 1963, including some unpublished data. Tables include some related compounds with normal moments, too. The part on factors controlling super-exchange is a guide for theoretical viewings. [The *SCI*® indicates that this paper has been cited in over 500 publications since 1964.]

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"The paper was prepared while I was a postdoctoral fellow with H.B. Jonassen at Tulane University in New Orleans. Then, I was engaged in work on copper(II) complexes with subnormal magnetic moments. Study in this field began with magnetic and structural investigations on copper(II) acetate monohydrate. The violent shock of finding the lantern type dimeric structure of this compound in 1953[1] was still in the minds of complex chemists. Were there any other groups of copper(II) compounds of dimeric structure with subnormal magnetic moments? This was an idea of magnetochemists at that time. It was realized by the finding of subnormal magnetic moments of so-called tricoordinated copper(II) complexes by Kishita, Muto, and Kubo in 1957.[2] Those compounds were prepared by Muto. Meanwhile, in 1961, the structure of one of these complexes, acetylacetonemono(o-hydroxyanil) copper(II), was determined, showing a planar phenolic oxygen bridged dimeric structure.[3] Under such circumstances, I went to Tulane in 1962. Jonassen wanted me to prepare a review paper (with Fanning). He emphasized that I should prepare the paper so that it would stimulate this young field of complex chemistry. Then, Muto came to Tulane in 1963 as another fellow with Jonassen. Sometimes, Jonassen came to my room to see the progress of my work. I always noticed his arrival in advance by the smell of his cigar which was characteristic of him. I appreciated the work of Cusachs, who contributed a theoretical viewpoint in Section V-C of the paper.

"The reasons why our paper has been frequently cited include: its timeliness, accuracy of tables and quoted references (one of the most important qualities for review papers), and the fact that it was written with foresight so as to stimulate the young field. The most important compounds in this field are copper(II) carboxylate dimers. However, the magnetic data from earlier times are often questionable and have caused confusion. Secondly, the exchange mechanism should be elucidated consistently not only with copper(II) acetates (singlet-triplet [S-T] separation, 300 cm^{-1}) but also with formates which have about twice as large S-T separations (500 cm^{-1}). At present, X-ray studies have shown that no particular bond lengths are contained in the latter compounds as once imagined.[4] Attention should be paid to Steward's complexes which contain silicon or germanium instead of carbon in copper(II) acetates as the element which directly binds to the carbon atom in the carboxylate bridges.[5] We confirmed that the S-T separations are about four times as large as acetates (1,200 cm^{-1}). The larger S-T separations of formates should be understood along this line where a hydrogen atom is bound to the carbon atom in the bridges. The origin of the band 27 kK which has been taken as characteristic of copper(II) acetate type complexes is still controversial.[6] Now, Muto, Steward, and I have got together to approach the most interesting unsolved problems under the idea as stated above. We welcome anyone who is interested in this extremely interesting subject, experimentally or theoretically. Subsequent review papers have appeared."[4,7-9]

1. **van Niekerk J N & Schoening F R L.** A new type of copper complex as found in the crystal structure of cupric acetate, $Cu_2(CH_3COO)_4.2H_2O$. *Acta Cryst.* **6**:227-32, 1953. (Cited 365 times.)
2. **Kishita M, Muto Y & Kubo M.** Magnetic susceptibility of tri-coordinated copper(II) complexes. *Aust. J. Chem.* **10**:386-91, 1957.
3. **Barclay G A, Harris C M, Hoskins B F & Kokot E.** The anomalous magnetic behaviour and binuclear structure of some so-called tri-coordinated copper(II) complexes. *Proc. Chem. Soc.* **1961**:264-5.
4. **Hay P J, Thibeault J C & Hoffmann R.** Orbital interactions in metal dimer complexes. *J. Amer. Chem. Soc.* **97**:4884-99, 1975. (Cited 115 times.)
5. **Steward O W & Piskor S R.** Dimeric copper(II) carboxylates with unusually low magnetic moments. *J. Chem. Soc. Chem. Commun.* **1973**:702-3.
6. **Kida S, Nishida Y & Sakamoto M.** Absorption band in the near-ultraviolet region observed for binuclear copper(II) complexes. *Bull. Chem. Soc. Jpn.* **46**:2428-30, 1973.
7. **Doedens R J.** Structure and metal-metal interactions in copper(II) carboxylate complexes. *Prog. Inorgan. Chem.* **21**:209-31, 1976.
8. **Hatfield W E.** Properties of magnetically condensed compounds (compounds with spin exchange). (Boudreaux E A & Mulay L N, eds.) *Theory and applications of molecular paramagnetism.* New York: Wiley, 1976. p. 349-449.
9. **Melnik M.** Study of the relation between the structural data and magnetic interaction in oxo-bridged binuclear copper(II) compounds. *Coord. Chem. Rev.* **42**:259-93, 1982.