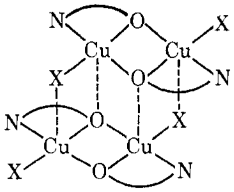
that J_C and J_B are small so that eq 3 collapses to eq 1. Thus, on the evidence available, the dimer model seems better than the tetramer and should not be discarded. The validity of the binuclear model is also important in the treatment of the antiferromagnetism of salicylaldimine complexes of copper halides, **4**, for which a weakly linked tetrameric structure was suggested although a binuclear interaction model was generally considered to be adequate.[18,25]



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Exchange Coupling Constants for Tetrametallic[1] Complexes[2]

Sir:

Sinn[3] has presented an analysis of the four-center exchange-coupled model which we[4] have suggested is appropriate for the description of the magnetic properties of the tetrametallic Schiff base complexes related to acetylacetonemono(*o*-hydroxyanil)copper(II). The tetrameric structure of the molecule was carefully described by Barclay and Hoskins[5] although the substance was called a dimer in the text of their paper and in the preliminary communication[6] of the magnetism and structure. This description has persisted.[7,8] It is common practice to ignore the out-of-plane copper–ligand interactions in the commonly seen "4 + 1" and "4 + 2" coordination of square-planar copper,[9] and it appears that it is this oversight which has led Sinn to his conclusions. It is our contention based on a variety of spectral and magnetic data[10] that such out-of-plane interactions cannot be ignored and that their neglect leads to a model which may be able crudely to account for the temperature variation of magnetism but which is fully incapable of describing the true nature of the magnetic interactions.

There are, of course, difficulties with the tetramer model, and it is accepted[11] that coupling constants derived from a model which neglects other important effects such as the orbital contribution to the magnetism and spin–orbit coupling are only first approximations. As Sinn[3] has pointed out, inclusion of these effects results in a proliferation of parameters and fitting processes become meaningless. These limitations, as originally noted by Kambe[12] in his early work on trimetallic chromium and iron carboxylates, do not render the treatment invalid but rather stimulate efforts toward the solution of the concomitant problems.

The evidence offered by Sinn in his critique concerns the dimer N,N′-ethylenebis(salicylaldimine)copper(II).[13] He noted that the "direct experimental evidence available...mitigates strongly against the tetranuclear (*sic*) model." We believe this statement to be premature since there are distinct structural and electronic differences between the two, and there are no empirical bases to guide or assess the transferability of coupling constants between molecules. In N,N′-ethylenebis(salicylaldimine)copper(II), the oxygen atom bridging the two copper(II) ions is bonded to only one other atom and has an unused lone pair of electrons, while in the tetramer acetylacetonemono(*o*-hydroxyanil)copper(II), the bridging oxygen atom is bonded to two other atoms (a third copper(II) ion and a carbon atom of the phenol ring). In addition there are structural differences[13a] in the four-member copper–oxygen ring which may have an important bearing on the mechanism of the magnetic interactions.

Detailed studies of copper complexes with out-of-plane "4 + 1" or "4 + 2" interactions are rare. Investigations which are germane to this discussion include that by Blumberg and Peisach,[14] who have shown that pairs of copper(II) ions in 3-ethoxy-2-ketobutyraldehydebis(thiosemicarbazone)copper(II) are exchange coupled giving a singlet ground state with a singlet–triplet splitting energy of 16 cm^{-1}. In this example, the square-planar complexes are linked into pairs by "4 + 1" coordination of the copper(II) ion to a sulfur atom in the adjacent molecule, and the out-of-plane copper–sulfur distance is 3.1 Å. Also, it has been shown[15] using low-temperature magnetic susceptibility measurements and electron paramagnetic resonance that the dimer $Cu_2(C_5H_5NO)_4(NO_3)_4$, which has structural features[16] in common with N,N′-ethylenebis(salicylaldimine)copper(II) and an out-of-plane Cu–O sep-

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[1] Henceforth, metal complexes containing two or more metal ions will be referred to as dimetallic, trimetallic, etc., instead of the more commonly used terms of dinuclear, trinuclear, ... Each atom in the complex has a nucleus and, consequently, the latter terms lack definition. In the context of this work the metal ions are, in most cases, the focus of attention, and the terms dimetallic, trimetallic, ..., are more appropriate.

[2] We are grateful for support of this research by the National Science Foundation under Grant GP-7400.

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aration of 2.4 Å, is exchange coupled with the triplet state lying lowest.

It is apparent that much experimental data must be collected on a variety of polymetallic complexes in well-characterized environments before the transferability of coupling constants can be used as a criterion for validity. However, once these empirical bases are established, *then* agreement between J values will be a useful test for the parameters which result from fitting processes. Thus, at this juncture, we reject Sinn's judgment.

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