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A New $FeCu_2$ Heterotrinuclear Complex $[Fe(Cuprp_2en)_2(ClO_4)_2(H_2O)_2]$. Definitive Evidence for a *cis*-Octahedral Configuration and an Isosceles Triangular Arrangement of Metal Atoms*

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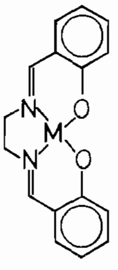
Trinuclear complexes containing paramagnetic transition metals were first prepared by the technique of using metal complexes as ligands [2–4]. Tetradentate Schiff base complexes of one metal (MTSB, 1) were reacted with a salt (such as perchlorate) of another, $M'(ClO_4)_n \cdot xH_2O$ to form oxygen bridged homo- or heterotrinuclear products, 2.



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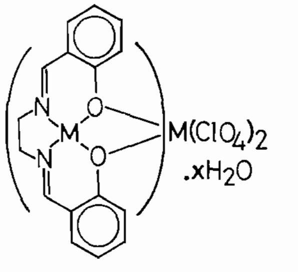

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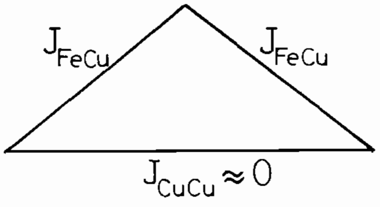

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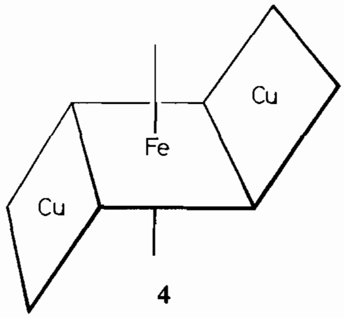
When all three metal atoms are paramagnetic, significant magnetic coupling is normally observed, principally between the adjacent metals M and M′, but not between the metals M inside the complex ligand. Thus if M = Cu, then M′ = Fe, $|J_{FeCu}| > 0$ and $J_{CuCu} \approx 0$. This can be represented by an isosceles triangle of coupling constants 3. A question which had remained unresolved was the particular arrangement of the metal atoms. This could be linear, based on a chair arrangement of the complex ligands bonded *trans* about the iron octahedron, 4, or triangular, based on either a boat configuration, 5, or a *cis*-octahedral coordination of the two complex ligands 6.



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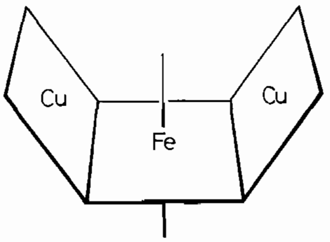

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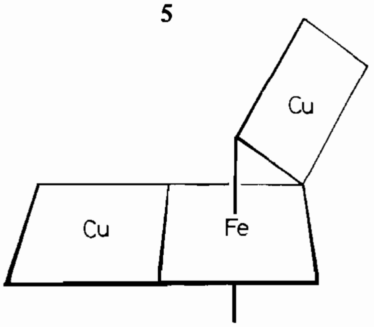

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Each configuration minimizes the steric strain that would result from attempts to fit two complex ligands in a coplanar arrangement, and each could produce the relative values of the coupling constants. Thus none of them is eliminated on steric or magnetic grounds.

Prompted by the considerable current interest in heteronuclear complexes in general, and iron–copper interactions in particular, we have synthesized a CuFeCu trinuclear complex, using a modified complex ligand, 1, $Cu(prp_2en)$ with ethyl substituents at the imine carbon atoms for improved solubility properties. The complex ligand, $Cu(prp_2en)$, was prepared from copper(II) acetate monohydrate, propiophenone, ethylenediamine and piperidine as previously described. The synthesis of the trinuclear complex was then also carried out according to literature methods by reacting equimolar amounts of

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*Metal Complexes as Ligands XIV. For Part XIII, see ref. 1.

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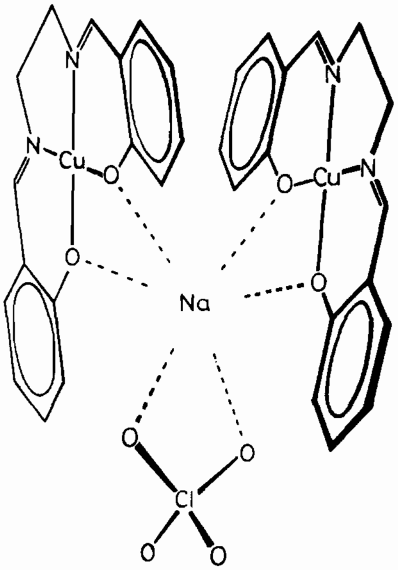
the hydrated metal perchlorate in methanol with the complex ligand in dichloromethane. This introduces an excess of Fe^{2+} and gives better results than when 2:1 stoichiometry is used. The resulting complex formed small crystals adequate for X-ray analysis, and one of these was selected for structure determination.

The space group is monoclinic, $C2/c$, with cell parameters $a = 10.136(3)$, $b = 22.22(2)$, $c = 20.476(10)$ Å, $\beta = 98.43(6)°$. Both the iron atom and a disordered CH_2Cl_2 solvent molecule both lie on a crystallographic special position, so that the asymmetric unit contains only one Cu(prp$_2$en) ligand. The main component of the crystal structure consists of the [Fe(Cu(prp$_2$en))$_2$(ClO$_4$)$_2$H$_2$O] molecule (7) together with a positionally disordered molecule of occluded solvent CH_2Cl_2. The trinuclear complex contains a central iron atom in a distorted octahedron with two Cu(prp$_2$en) complex ligands in a *cis* configuration. The remainder of the octahedron is completed by coordinated water molecules. The copper atoms in the complex ligands have a semi-coordinated perchlorato group in the fifth position. The complex ligand is coordinated slightly asymmetrically to the central iron: the two independent Fe–ligand oxygen distances are 2.06 and 2.18 Å, while the equivalent Fe–water oxygen distances are 2.12 Å. The Fe–Cu separation is 2.976 Å, rather similar to the distances observed in the related binuclear complexes 7 with M = Cu. These are 3.03, 2.96 and 3.00 Å when M′ = Cu, Co [4] and Fe [5] respectively.



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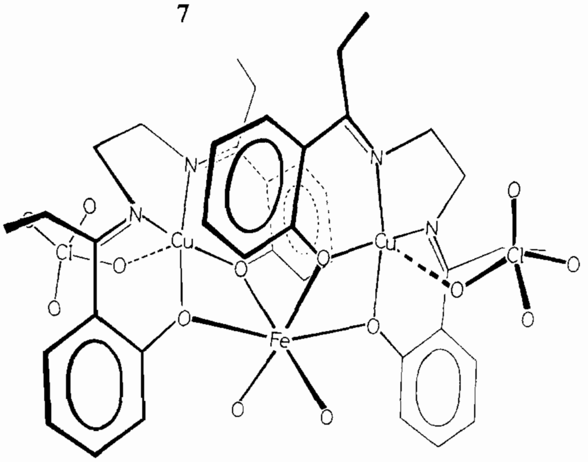

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Clearly the structure of complex 7 is of the *cis*-octahedral type analogous to **6**. It resembles the uncoupled member of the series that has been examined structurally, [Na(CuES)$_2$ClO$_4$] (**8**) [6], although the sodium was not considered to be coordinated so that it was not clear whether **8** was a true member of the trinuclear series. It is now apparent that 7 and **8** are analogous, and the *cis*-octahedral structure **6** appears to be the optimal way to overcome the steric problems of fitting two complex ligands on to a central metal atom.

Acknowledgement

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References

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