

**Ferromagnetic Coupling and Electron Transfer in $\text{CoCu}(\text{ben})\cdot 3\text{H}_2\text{O}$
[$\text{H}_4\text{ben} = \text{NN}'$ -Bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane]†**

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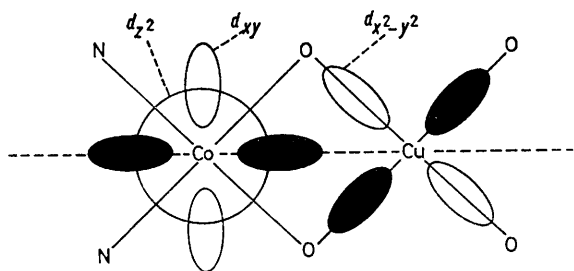
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Summary The title heterobinuclear complex exhibits a very strong ferromagnetic coupling due to the orthogonality of the magnetic orbitals; it can also show the intramolecular electron transfer $\text{Co}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Co}^{\text{III}}\text{Cu}^{\text{I}}$.

IN binuclear complexes with paramagnetic metallic centres, the exchange interaction parameter J which appears in the Heisenberg–Dirac–Van Vleck Hamiltonian, whatever its sign may be, is interpreted as resulting from an antiferromagnetic component J_{AF} and a ferromagnetic component

† In refs. 1 and 4, the abbreviation $\text{H}_4(\text{fsa})_2\text{en}$ was used for this ligand.

J_F . Although the mechanism of the antiferromagnetic coupling is well understood, that of the ferromagnetic coupling is not clear. The synthesis and study of the magnetic properties of binuclear complexes, in which the magnetic orbitals centred on the transition metal ions are strictly orthogonal, should enable us to understand the main factors governing the magnitude of J_F since in such complexes J_{AF} is zero. The first complex of this type was recently reported.¹ Here we describe a new complex of this kind, $\text{CoCu}(\text{ben})\cdot 3\text{H}_2\text{O}$ [$\text{H}_4\text{ben} = \text{NN}'\text{-bis}(2\text{-hydroxy-3-carboxybenzylidene})\text{-1,2-diaminoethane}\dagger$], in which the ferromagnetic coupling is, to our knowledge, the strongest found so far.



The synthesis is carried out in two steps. First the mononuclear complex $\text{Co}(\text{H}_2\text{ben})\cdot 2\text{H}_2\text{O}\ddagger$ is prepared by the action of $\text{Co}(\text{MeCO}_2)_2\cdot 4\text{H}_2\text{O}$ on H_4ben in methanol at reflux under nitrogen. The complex $\text{CoCu}(\text{ben})\cdot 3\text{H}_2\text{O}\S$ is then prepared by action of $\text{CuCl}_2\cdot 6\text{H}_2\text{O}$ on the lithium salt of $\text{Co}(\text{H}_2\text{ben})\cdot 2\text{H}_2\text{O}$ in methanol under nitrogen; small bright-brown crystals of the complex are obtained by slow evaporation of the solvent. X-Ray and i.r. studies show that this $[\text{CoCu}]$ complex with the Co and Cu atoms occupying the $-\text{N}_2\text{O}_2$ and $-\text{O}_2\text{O}_2$ sites, respectively, does not contain any detectable amount of the $[\text{CuCo}]$ isomer in which the positions of the metal atoms are reversed.²

The temperature dependence of the magnetic susceptibility χ_M of the complex $\text{CoCu}(\text{ben})\cdot 3\text{H}_2\text{O}$ was studied in the range $3.6 < T/\text{K} < 300$. Between 30 and 300 K, χ_M closely follows a Curie law $\chi_M T = 1.69 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (the diamagnetism is estimated as $-238 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$

and the T.I.P. as $170 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$). Below 30 K, $\chi_M T$ slowly decreases to $1.55 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 3.6 K, this low temperature behaviour being most likely due to a weak intermolecular antiferromagnetic coupling. The Curie behaviour for $T > 30 \text{ K}$ means that only one molecular level is populated in the whole temperature range. If the single-ion ground term for the Co^{II} ion was a spin quartet, the variation of $\chi_M T$ with T would be similar to that obtained with the $[\text{CuCo}]$ complex; $\chi_M T$ would continuously decrease from ca. $2.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ to a very low value upon cooling from room temperature to pumped helium temperature.³ Therefore, it may be asserted that the single-ion ground term for the Co^{II} ion is a spin doublet. In such a case, the unpaired electron would be in a $d_{xy} + d_{z^2}$ orbital, symmetrical with regard to the mirror-plane perpendicular to the molecular plane, whereas the unpaired electron around the Cu^{II} ion would be a $d_{x^2-y^2}$ orbital antisymmetrical with regard to the same mirror-plane.⁴ The two magnetic orbitals are strictly orthogonal and the exchange interaction should be ferromagnetic in nature. The value of the Curie constant confirms that the molecular ground state is the spin triplet arising from the ferromagnetic interaction between two single-ion spin doublets. The molecular spin singlet is too high in energy to be significantly populated and the value of the J parameter is of several hundreds of wavenumbers.

By modifying the reaction conditions, we obtained samples of the complex having the same chemical composition, but with magnetic susceptibilities varying according to laws $\chi_M T = 1.69 k$ with $0.4 < k < 1$. This peculiar behaviour is interpreted as resulting from the presence of the paramagnetic pair $\text{Co}^{\text{II}}\text{Cu}^{\text{II}}$ and the diamagnetic pair $\text{Co}^{\text{III}}\text{Cu}^{\text{I}}$, the latter arising from the intramolecular transfer of the unpaired electron around the Co^{II} ion to the $d_{x^2-y^2}$ magnetic orbital centred around the Cu^{II} ions. Heating any of these samples in a tube sealed under vacuum resulted in an increase in $\chi_M T$ to a maximum value of $1.69 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at room temperature. Thus, on heating we are able to displace the equilibrium in the solid phase $\text{Co}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Co}^{\text{III}}\text{Cu}^{\text{I}}$.

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† Satisfactory C, H, and N analyses were obtained for this complex.

§ Satisfactory C, H, Co, Cu, and N analyses were obtained for this complex.

¹ O. Kahn, P. Tola, J. Galy, and H. Coudanne, *J. Amer. Chem. Soc.*, 1978, **100**, 3931.

² H. Okawa, Y. Nishida, M. Tanaka, and S. Kida, *Bull. Chem. Soc., Japan*, 1977, **50**, 127.

³ O. Kahn, P. Tola, and H. Coudanne, unpublished results.

⁴ P. Tola, O. Kahn, C. Chauvel, and H. Coudanne, *Nouveau J. Chim.*, 1977, **1**, 467.