

[s9.m1.p9] Zerovalent copper in reactions with triethanolamine and cobalt(II) salts: syntheses, structural, spectroscopic and magnetic studies of novel mixed-metal Cu/Co complexes. V.G. Makhankova,^a O.Yu. Vassilyeva,^a V.N. Kokozay,^a B.W. Skelton^b, ^a *Chemistry Dpt, National Taras Shevchenko University, Volodymirska st. 64, Kyiv 01033, Ukraine,* ^b *Chemistry Dpt, University of Western Australia, Nedlands, Western Australia 6907, Australia*

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Reaction of zerovalent copper with cobalt(II) salts and triethanolamine (H₃Tea) in air yielded three novel mixed-metal complexes: the unique pentanuclear mixed-valence complex [Cu⁰₂Co²⁺₂(O₂CMe)₄(H₂Tea)₂(Tea)₂·2(HO₂CMe) **1** and mononuclear compounds [CuCo(H₂Tea)₂X₂] **2** (X = SCN) and **3** (X = Cl) that have been characterised by a range of spectroscopic methods. **1** and **2** have been studied structurally, a preliminary report of the structure of **3** is also given. In the pentanuclear unit of **1**, which has an inversion centre, five metals ions are linked together by ten oxygen atoms of the four triethanolamine ligands and two acetate anions in the sequence Cu(II)-Co(III)-Co(II)-Co(III)-Cu(II) with the metal-metal separations of 2.823(2) and 2.964(1) Å for Cu(II)-Co(III) and Co(III)-Co(II), respectively. The intermolecular hydrogen bonding links the pentanuclear units together and results in the formation of an extended one-dimensional structure. The hydrogen-bonded network involving the nonco-ordinating acetic acid molecules is believed to be essential for the complex entity.

The simultaneous presence of copper and cobalt in **2** and **3** was unambiguously determined by atomic absorption, EPR and electronic spectroscopy. The mononuclear complexes **2** and **3** contain crystallographically indistinguishable Cu(II) and Co(II) ions in identical trigonal bipyramidal sites. Two oxygen atoms from the two ethanol groups and one from the ethanolato group form the basal plane with nitrogens occupying the apical positions. The shortest metal-O bond length is attributed to the negative charge on the oxygen atom in the C₂H₄O⁻ group. The base angles of the equatorial plane are close to 120°, thus approximating to C₃ symmetry. The metal atom does not lie in the plane of oxygen atoms but is shifted towards the N_{SCN} (**2**). The molecules are linked together by O-H...O hydrogen bonds to give chains parallel to the *b* axis.

C₃₆H₇₂Co₃Cu₂N₄O₂₄, *M* = 1248.87, triclinic, *a* = 7.181(2), *b* = 12.321(2), *c* = 14.958(3) Å, α = 88.55(2), β = 83.61(2), γ = 86.50(2)°, *U* = 1312.5(5) Å³, *T* = 293 K, *P* $\bar{1}$, *Z* = 1, μ (Mo-K α) = 1.806 mm⁻¹, 5019 reflections measured, 4615 unique (*R*_{int} = 0.0360), 3005 observed (*I* > 2 σ (*I*)). The final *R*, *R*_w were 0.062, 0.066.

C₇H₁₄Cu_{0.5}Co_{0.5}N₂O₃S, *M* = 267.51, orthorhombic, *a* = 10.682(3), *b* = 7.963(2), *c* = 12.391(3) Å, *U* = 1054.0(5) Å³, *T* = 150 K, *Pnma*, *Z* = 4, μ (Mo-K α) = 2.031 mm⁻¹, 12300 reflections measured, 1444 unique (*R*_{int} = 0.055), 1219 observed (*F* > 4.00 σ (*F*)). The final *R*, *R*_w were 0.044, 0.052.

[s9.m1.p10] Temperature And Pressure Dependence Of The Crystal Structures Of Spin Crossover Iron Complexes. M. Marchivie, P. Guionneau, M. Kollmannsberger, J.F. Létard, Y. Barrans, A.E. Goeta*, J.A.K. Howard*, D. Chasseau. *Institut de Chimie de la Matière Condensée de Bordeaux, CNRS UPR 9048, 87 Av. Dr A. Schweitzer, 33608 Pessac Cedex, France.* **Chemical Crystallography group, University of Durham, Durham DH13LN, U.K.*

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This spin crossover phenomenon derives from the existence of two different configurations for the metallic ion characterised by different spin states. For example, in d⁶ metal complexes of Fe(II), it corresponds to the change in the population of the 3d orbitals from the high spin state t_{2g}⁴e_g² (HS) to the low spin state t_{2g}⁶e_g⁰ (LS). Such a transition may be induced by thermal changes, pressure effects or exposure to electromagnetic rays and be smooth or abrupt, accompanied or not, with a hysteresis phenomenon. It corresponds to a drastic change in the Fe environment geometry. Our aim is to correlate the intramolecular and intermolecular structural properties to the features of the spin transition and to elucidate the role played by the pressure and the temperature.

We have been investigating the Fe(NCS)₂(PM-X)₂ spin crossover series for a few years. In the present communication, we will review our results and try to enhance some general trends based on the determination of around twenty crystal structures determined at various pressures (up to 6 kbar) and temperatures (down to 10 K).