A unique heteropentanuclear $Cu^{II}{}_2Co^{II}Co^{III}{}_2$ complex, synthesised from metallic Cu and Co acetate in the presence of triethanolamine. Magnetic properties and a strong H-bond stabilised lattice

Valeriya G. Makhankova,[a] Olga Yu. Vassilyeva,*[a] Volodymyr N. Kokozay,[a] Brian W. Skelton,[b] Jan Reedijk,[c] Gerard A. Van Albada,[c] Lorenzo Sorace[d] and Dante Gatteschi[d]

[a] *Department of Inorganic Chemistry, National Taras Shevchenko University, Volodimirska st. 64, Kyiv, 01033 Ukraine. E-mail: vassilyeva@chem.univ.kiev.ua; Fax: +380 44 296 2467*
[b] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia, 6907, Australia*
[c] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands*
[d] *Department of Chemistry, University of Florence, via Maragliano 77, 50144 Florence, Italy*

Received (in Montpellier, France) 15th November 2000, Accepted 23rd January 2001
First published as an Advance Article on the web 12th April 2001

Reaction of zerovalent copper with cobalt(II) acetate and triethanolamine (H_3Tea) in DMF solution in air yields the unique pentanuclear mixed-valence complex $[Cu^{II}{}_2Co^{II}CO^{III}{}_2(O_2CMe)_4(H_2Tea)_2(Tea)_2]\cdot 2(HO_2CMe)$, **1**, which has been characterized by a range of spectroscopic methods and structurally by X-ray crystallography. In the centrosymmetric unit of **1** five metal ions are linked together by eight oxygen atoms of the four triethanolamine ligands and by two acetate anions in the sequence Cu(II)–Co(III)–Co(II)–Co(III)–Cu(II), with the metal–metal separations being 2.823(2) and 2.964(1) Å for Cu(II)···Co(III) and Co(III)···Co(II), respectively. Discrimination between Co(II) and Co(III) atoms is based on bond length considerations; the Co(III) is low spin. The lattice hydrogen-bonded network involving the non-coordinating acetic acid molecules links the pentanuclear units together and results in the formation of an extended one-dimensional structure. Magnetic measurements for **1** showed a marked decrease of the χT value at low temperature, indicative of antiferromagnetic interactions between magnetic centres. A fit was attempted assuming an effective $S = 1/2$ ground state for Co(II) and an Ising-type anisotropy, considering only intramolecular interactions. The obtained value for J_z of 36 cm^{-1} must originate from the efficient role of the diamagnetic Co(III) in transmitting the interaction between Cu(II) and Co(II) below 40 K.

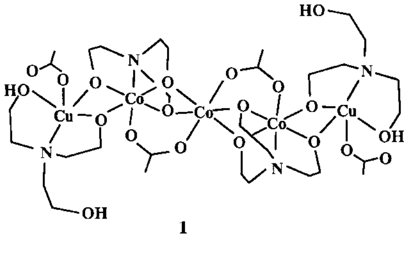
The study of polynuclear metal complexes is one of the most active areas in coordination chemistry. These compounds constitute common ground for two areas of current interest, molecular magnetism and metal sites in biology. The detection of magnetic exchange coupling between paramagnetic metal centres has been particularly useful in deducing the structures of polynuclear metal compounds and the active sites of much larger metallobiomolecules.[1] Our synthetic approach to the preparation of coordination compounds employing zerovalent metals as starting materials[2] has proved to be an efficient route to novel mixed-metal complexes. In previous papers, we reported the structures and properties of mixed-metal tri- and tetranuclear Cu/Pb complexes prepared from copper powder and lead halide in non-aqueous solutions of amino alcohols in air.[3] The copper oxidation and complex formation were conditioned by the presence of a proton-donating agent (amino alcohol) and dioxygen from the air *via* the following reaction in which the water molecule was usually the only by-product:

$$Cu^0 + PbX_2 + 2\,HL + 1/2\,O_2 \xrightarrow{\text{solv.}} CuPbX_2L_2 + H_2O \quad (1)$$

with X = Cl, Br, I, SCN; solv. = DMF, DMSO, CH_3CN, CH_3OH; HL = 2-aminoethanol, 2-dimethylaminoethanol. The X-ray crystal structures showed that metal ions are bridged by alkoxo oxygens of the amino alcohols and by halide or thiocyanate ligands.

Of particular interest from the standpoint of studies of geometry and exchange mechanism are new spin systems that can be formed in reactions with zerovalent metal. This reaction route can produce complexes of unusual stoichiometry and structure, and even some that would not have been thought of as capable of existing.[4] The subtle interactions that control the formation of complexes in such conditions and their architectural characteristics may be rationalised after the event, but can rarely be predicted in advance.

Following our extensions of the earlier studies, we have used triethanolamine as a ligand reported to be able to achieve control of the stoichiometry and geometry of mixed-metal species.[5] Herein we describe our latest efforts to correlate the magnetic and structural properties of the novel mixed-metal mixed-valence pentanuclear complex $[Cu^{II}{}_2Co^{II}Co^{III}{}_2(O_2CMe)_4(H_2Tea)_2(Tea)_2]\cdot 2(HO_2CMe)$, **1**, resulting from the interaction of zerovalent copper with cobalt(II) acetate and triethanolamine [H_3Tea, $N(C_2H_4OH)_3$] in solution in air. Details of the synthesis, crystal structure, spectroscopic investigations as well as magnetostructural correlations of the compound that provide evidence for an efficient role of the diamagnetic Co(III) in transmitting the interaction between Cu(II) and Co(II) at the low temperature are presented.



1

DOI: 10.1039/b009194o

Experimental

Synthesis

Commercial reagents were used without further purification; all experiments were carried out in air. $[Cu_2Co_3(O_2CMe)_4(H_2Tea)_2(Tea)_2]\cdot 2(HO_2CMe)$ (**1**) was obtained as follows: copper powder (0.32 g, 5 mmol), $Co(O_2CMe)_2\cdot 4H_2O$ (1.60 g, 7.5 mmol), DMF (20 cm^3) and triethanolamine (1.33 cm^3, 10 mmol) were heated to 60 °C and magnetically stirred until total dissolution of Cu^0 and $Co(O_2CMe)_2\cdot 4H_2O$ was observed (4 h). The red–brown solution gradually turned intense brown. The gradual addition of Pr^iOH into the resulting solution allowed the isolation of brown–pink crystals of **1** suitable for an X-ray crystallographic study. They were filtered out, washed with Pr^iOH and finally dried *in vacuo* at room temperature. Yield: 1.6 g, 51%. IR data (KBr, cm^{-1}): 3600–3350br, 3208–3230br, 2990w, 2965w, 2930sh, 2915m, 2880sh, 2860m, 2830m, 1650s, 1595s, 1485w, 1455sh, 1440sh, 1425s, 1395sh, 1370m, 1295m, 1255w, 1220w, 1130w, 1090s, 1060s, 1045s, 1015sh, 940w, 910w, 900m, 720w, 695w, 660w, 650w, 620w, 590w, 560sh, 545w, 530m, 515w, 495w, 455w, 435w. Elemental analyses for metals were performed by atomic absorption spectroscopy and potentiometric titration with a solution of $K_3[Fe(CN)_6]$ for Co(II).[6] Elem. anal. found: C, 34.5; H, 5.7; N, 4.7; Cu, 10.2; Co_{total}, 14.2, Co^{II}, 5.1; calc. for $C_{36}H_{72}Co_3Cu_2N_4O_{24}$: C, 34.62; H, 5.81; N, 4.49; Cu, 10.18; Co_{total}, 14.16, Co^{II}, 4.72%. The compound is soluble in water and sparingly soluble in common organic solvents; it is stable in air for periods of months.

Physical measurements

The IR spectrum (4000–400 cm^{-1}) was recorded on a KBr pellet with a UR-10 spectrophotometer. UV/Vis spectra were recorded on Perkin Elmer 330 (diffuse-reflectance technique) and "LOMO" adapted for IBM PC spectrophotometers (DMF solution spectrum in the visible region). X-Band DMF frozen solution and solid-state EPR spectra at 77 K were measured with a JEOL RE2x spectrometer using an ESR900 continuous-flow cryostat. Magnetic susceptibility was measured in the temperature range 4–300 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *ca.* 1.4 T. Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Crystal structure determination

All measurements were performed on an Enraf–Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode equipped with graphite-monochromated Mo-Kα radiation (Table 1). The data were collected to a maximum 2θ value of 50°. The data were corrected for Lorentz polarisation effects and for the effects of absorption (Gaussian). The structure was solved by direct methods using the SHELXS 86[7] program and refined by full-matrix least-squares methods on *F* using SHELXL 93[8] and XTAL3.4.[9] The non-hydrogen atoms were refined anisotropically, hydrogen atoms were included but not refined. Largest difference peak and hole were 0.974 and -0.778 Å^{-3}.

The C(17), C(18), O(11) and O(12) atoms of the solvent molecule in **1** show substantial thermal displacement parameters, possibly caused by some degree of disorder or the poor quality of the crystal. Efforts to model this disorder were unsuccessful. On the other hand, the disorder of O(6) was modelled successfully in terms of two positions, O(6A) and O(6B), each occupancy fixed at 0.5 after initial refinement. An acidic proton for the solvent molecule and OH protons for the monodeprotonated triethanolamine ligand in **1** were not located. The bond distances and angles of the H_3Tea groups are normal and are given as electronic supplementary information.

Table 1 Crystal data and structure refinement of the title compound

Empirical formula	$C_{36}H_{72}Co_3Cu_2N_4O_{24}$
Formula weight	1248.87
Crystal system	Triclinic
Crystal group	$P\bar{1}$
a/Å	7.181(2)
b/Å	12.321(2)
c/Å	14.958(3)
α/°	88.55(2)
β/°	83.61(2)
γ/°	86.50(2)
U/Å^3	1312.5(5)
Z	1
λ/Å	0.710 73
T/K	293
μ/cm^{-1}	18.06
Total reflections	5019
Unique reflections ($R_{int} = 0.0360$)	4615
Observed reflections [$I > 2\sigma(I)$]	3005
Final R indices [$I > 2\sigma(I)$]	$R = 0.062$, $wR = 0.066$

CCDC reference number 153397. See http://www.rsc.org/suppdata/nj/b0/b009194o/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

When copper powder and cobalt(II) acetate are treated with a DMF solution of triethanolamine in air dissolution of copper is accomplished in 4 h and a mixed-metal compound is obtained, which shows analytical data accounting for the presence of Cu(II), Co(II) and Co(III) in a 2 : 1 : 2 stoichiometry. The ratio of metals in the reaction mixture does not appear to influence the reaction product. The title compound could also be isolated as a pure product from DMSO and methanol solutions. Factors that govern the nuclearity of the complex include the ligand nature of the amino alcohol and acetate, the nature of the transition metals involved, and the stability and solubility of complex species.

Considering the analytical results, one could theoretically infer 5 possible formulations for this compound, depending on whether the $(H)O_2CMe$ ligands are O_2CMe^- ions or HO_2CMe molecules and whether the OH groups of the amino alcohol are alkoxo or hydroxo functions. These formulae are $Cu^{II}_2Co^{II}Co^{III}_2(O_2CMe)_6(HTea)_2(H_2Tea)_2$, $Cu^{II}_2Co^{II}Co^{III}_2(O_2CMe)_6(Tea)_2\cdot 2(H_3Tea)$, $Cu^{II}_2Co^{II}Co^{III}_2(Tea)_4\cdot 6(HO_2CMe)$, $Cu^{II}_2Co^{II}Co^{III}_2(O_2CMe)_4(HTea)_4\cdot 2(HO_2CMe)$ and $Cu^{II}_2Co^{II}Co^{III}_2(O_2CMe)_4(H_2Tea)_2(Tea)_2\cdot 2(HO_2CMe)$. Given the hydrogen bonding in the lattice (see below), whereby acetic acid molecules link the clusters in chains, and given the unambiguous valence state assignments for the metal ions (see below), the formula as given in **1** can be deduced.

In order to determine whether the method of preparation has a profound effect upon the formation of **1** we attempted to prepare it by a conventional synthesis. Copper(II) and cobalt(II) acetate hydrates were dissolved in DMF and triethanolamine was added to the reaction mixture (molar ratio 1 : 1.5 : 2). The successive addition of isopropanol into the resulting dark solution led to precipitation of a light blue crystalline product that appeared to be a copper(II) acetate complex with triethanolamine of the general formula

$Cu(H_2Tea)(O_2CMe)$, according to elemental analyses and IR spectroscopy.

Spectroscopic measurements

The infrared spectrum of the crystalline complex **1** displayed several intense bands not observed in the spectra of copper and cobalt complexes of this ligand with other anions[10] at 1650, 1595, 1440, 1425 and 1295 cm^{-1} and therefore assigned to $\nu(CO_2)$ frequencies. Consideration of infrared data for known carboxylate complexes suggested the presence of at least two different coordination modes for the acetate ligand as well as the presence of uncoordinated acetate moieties.[11] Separations between $\nu(CO_2)$ frequencies of 155 cm^{-1} (bands at 1595 and 1440 cm^{-1}) and 225 cm^{-1} (bands at 1650 and 1425 cm^{-1}) allow us to predict bridging and unidentate carboxylate coordination, respectively. The sharp band of medium intensity at 1295 cm^{-1} can reasonably be assigned to a $\nu(CO) + \delta(OH)$ combination band of "free" acetic acid.[12]

The electronic spectral data for **1** were traced back to those of cobalt(III) complexes with triethanolamine,[13a] as well as trinuclear mixed-valence compounds of the overall formula $[Co^{II}\{Co^{III}(chelate)_3\}_2]^{m+}$.[13b] The DMF solution electronic spectrum of **1** exhibits the low-energy absorption (563 nm), attributable to a transition in the visible region of a low-spin cobalt(III) in octahedral geometry, obscuring the transitions of the divalent metal ions. In the solid state two major bands are observed at 561 and 784 nm. The former, almost unshifted from the solution spectrum, is assigned to a cobalt(III) centre. The band at 784 nm, which is not detectable in solution because it falls near the limit (800 nm) to which our spectrophotometer can measure, is assigned to a five-co-ordinate copper(II) centre revealed in the crystal structure.[14] The high energy, very intense band at 368 nm is associated with a charge-transfer transition. Bands from Co(II) LF transitions are assumed to be too weak to be visible.

The powdered EPR spectrum of **1** at room temperature displays a very weak broad signal of linewidth nearly 300 G centered at *ca.* $g = 2.13$; the frozen solution spectrum in DMF consists of well-resolved and easily identifiable parallel components of the Cu(II) hyperfine splitting (the fourth component seems to have merged with the strong absorption in the $g_\perp$ region). The perpendicular components are not resolved. The observed $g_\parallel = 2.18$, $A_\parallel = 126.4 \times 10^{-4}$ cm^{-1} and $g_\perp = 2.06$ (the average g value is 2.14) for **1** are in accord with the $d_{x^2-y^2}$ orbital as the ground state[14] for a Cu(II) ion in solution. Agreement between spectroscopic parameters for **1** in the solid state and solution lends support to a conclusion that the solid-state and solution coordination geometries at the metal centres are similar although it does not provide strong evidence that the pentanuclear structure is retained in DMF. No EPR signals originating from Co(II) are visible under these conditions, due to relaxation.[15]

Crystal structure

The complex consists of the pentanuclear unit $[Cu^{II}_2Co^{II}Co^{III}_2(O_2CMe)_4(H_2Tea)_2(Tea)_2]$, which has an inversion centre (Fig. 1) and two molecules of acetic acid in the crystal lattice. The five metal ions are linked together by eight oxygen atoms of the four triethanolamine ligands and by two acetate anions with the metal–metal separations being 2.823(2) and 2.964(1) Å for Cu(1)···Co(2) and Co(2)···Co(3), respectively. None of these distances is sufficiently short to imply any metal–metal bonding. The bridging acetato or carboxylato ligand has been a subject of considerable recent studies and both single and multiple bridges are known and have been reported from our labs before,[16] as well as some chained species.[16c] Our assignments of the positions of metal ions are based on the relative metal–N(O) bond distances and the geometric features of the three chromophores. The assumption of a neutral acetic acid that follows from counting the electrostatic charges and is confirmed by IR spectroscopy cannot be verified structurally, however. Nevertheless, the proposed formulation is the only plausible one when the method of preparation and various features of the structure are taken into account. Although the formation of acetic acid can be understood if one considers the following reaction scheme,

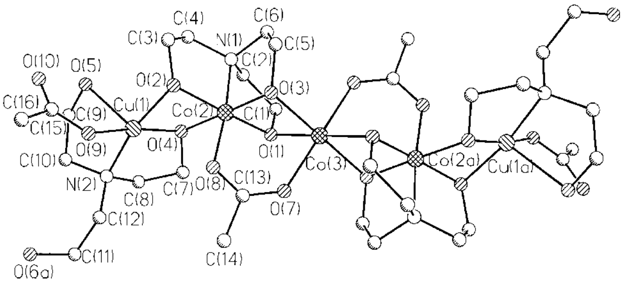


Fig. 1 Structure of the pentanuclear unit in the crystal structure of **1** [H atoms omitted for clarity, one position of the disordered O(6) atom shown].

$$2\,Cu^0 + 3\,Co(O_2CMe)_2 + 4\,H_3Tea + 1.5\,O_2 \xrightarrow{DMF}$$

$$Cu_2Co_3(O_2CMe)_4(H_2Tea)_2(Tea)_2 + 2\,HO_2CMe + 3\,H_2O \quad (2)$$

its presence in the crystal structure in an uncoordinated form was unexpected. Its role as an H-bonding species appears to be at the origin of this behaviour.

The divalent cobalt ion, Co(3), is located at the centre of inversion, and its coordination geometry can be best described as a slightly distorted octahedron. The four bridging alkoxo oxygens of triethanolamine are coordinated in a plane and the remaining coordination sites are occupied by the bridging acetate oxygens. The geometry at the trivalent cobalt ions, Co(2) and Co(2a), is a near octahedron with the Co(2)–O(N) distances, 1.885(5)–1.952(6) Å (Table 2), comparable to those of low-spin cobalt(III) in an octahedral environment.[17]

The atom Cu(1) is five-coordinate with a square-pyramidal geometry. The four copper–ligand bonds in the plane have normal bond distances, while the axial Cu–O(5) bond is elongated [2.436(6) Å] owing to the Jahn–Teller effect in the d^9 electronic configuration (Table 2). This long distance also allows one to presume the hydroxo donor function of the O(5) oxygen atom. The deviation of the Cu from the basal NO_3 least-squares plane toward O(5) is 0.147(1) Å.

The uncoordinated oxygen atom of the acetate ligand forms an intramolecular hydrogen bond with the OH group of the H_2Tea^- ligand Fig. 2, as evidenced by the O(10)–O(5) distance of 2.631(1) Å. Bond distances within acetate ligands are unremarkable (Table 2). Two non-coordinating acetic acid molecules are connected to complex **1** *via* hydrogen bonds (see Fig. 2) between the OH groups of the acetic acid and H_2Tea^- ligand and O(10) atom of the acetate ligand, as indicated by the relatively short distances of O(11)–O(6) $\{-x, 1-y, 1-z\}$ [2.79(2) and 2.74(3) Å for O(6A) and O(6B) atoms, respectively] and O(11)–O(10) [2.74(1) Å]. The intermolecular hydrogen bonding links the pentanuclear units together and results in the formation of an extended one-dimensional structure (Fig. 2).

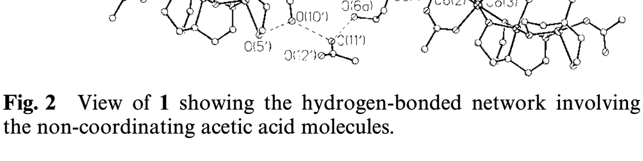


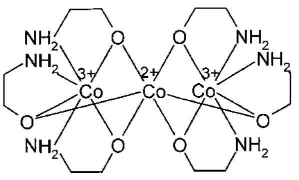
Fig. 2 View of **1** showing the hydrogen-bonded network involving the non-coordinating acetic acid molecules.

Table 2 Selected bond distances (Å) and angles (°) for **1**[a]

Metal coordination spheres			
Cu(1)–O(2)	1.961(5)	Co(2)–O(3)	1.885(5)
Cu(1)–O(4)	1.908(5)	Co(2)–O(4)	1.913(5)
Cu(1)–O(5)	2.436(6)	Co(2)–O(8)	1.928(6)
Cu(1)–O(9)	1.940(7)	Co(2)–N(1)	1.914(7)
Cu(1)–N(2)	2.053(7)	Co(3)–O(1)	2.107(5)
Co(2)–O(1)	1.890(6)	Co(3)–O(3)	2.087(5)
Co(2)–O(2)	1.952(6)	Co(3)–O(7)	2.113(6)
O(2)–Cu(1)–O(4)	81.2(2)	O(2)–Co(2)–O(3)	98.0(2)
O(2)–Cu(1)–O(5)	105.8(2)	O(2)–Co(2)–O(4)	81.3(2)
O(2)–Cu(1)–O(9)	95.5(2)	O(2)–Co(2)–O(8)	86.9(2)
O(2)–Cu(1)–N(2)	166.0(3)	O(2)–Co(2)–N(1)	87.6(3)
O(4)–Cu(1)–O(5)	97.9(2)	O(3)–Co(2)–O(4)	179.3(2)
O(4)–Cu(1)–O(9)	168.1(2)	O(3)–Co(2)–O(8)	94.0(2)
O(4)–Cu(1)–N(2)	85.4(3)	O(3)–Co(2)–N(1)	89.2(2)
O(5)–Cu(1)–O(9)	94.0(3)	O(4)–Co(2)–O(8)	86.4(2)
O(5)–Cu(1)–N(2)	79.8(3)	O(4)–Co(2)–N(1)	90.4(2)
O(9)–Cu(1)–N(2)	96.9(3)	O(8)–Co(2)–N(1)	174.0(3)
O(1)–Co(2)–O(2)	173.5(2)	O(1)–Co(3)–O(3)	75.9(2)
O(1)–Co(2)–O(3)	86.2(2)	O(1)–Co(3)–O(7)	85.7(2)
O(1)–Co(2)–O(4)	94.4(2)	O(1)–Co(3)–O(3′)	104.1(2)
O(1)–Co(2)–O(8)	97.8(2)	O(1)–Co(3)–O(7′)	94.3(2)
O(1)–Co(2)–N(1)	87.5(3)	O(3)–Co(3)–O(7)	87.3(2)
Acetate groups			
O(7)–C(13)	1.23(1)	C(15)–C(16)	1.49(2)
O(8)–C(13)	1.26(1)	O(11)–C(17)	1.36(3)
C(13)–C(14)	1.51(1)	O(12)–C(17)	1.33(4)
O(9)–C(15)	1.25(1)	C(17)–C(18)	1.37(4)
O(10)–C(15)	1.24(1)	O(10)–C(15)–C(16)	118(1)
O(7)–C(13)–O(8)	126.3(9)	O(11)–C(17)–O(12)	119(3)
O(7)–C(13)–C(14)	119.0(8)	O(11)–C(17)–C(18)	116(3)
O(8)–C(13)–C(14)	114.7(8)	O(12)–C(17)–C(18)	114(2)
O(9)–C(15)–O(10)	124(1)		
O(9)–C(15)–C(16)	117(1)		

[a] Atoms designated ′ are related by the symmetry operation $1 - x, -y, -z$.

It is interesting to compare the structures of the trinuclear cobalt "core" in **1** and compounds of the overall formula $[Co^{II}\{Co^{III}(chelate)_3\}_2]^{m+}$. For example, in the complex cation[18a] of $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}Cl_3 \cdot NH_3CH_2CH_2OH \cdot 2H_2O$,



amino alcohols form two octahedral tris-chelating complexes with the two Co(III) atoms, which are bridge-bonded by Co(II) into a trinuclear fragment through six oxygen atoms. This arrangement of cobalt(II,III) and oxygen atoms found in complexes prepared both from Co(II)[18a,b] and Co(III)[18c] salts is evidently very stable and one can presume that its formation is so advantageous that initial Co(II) or Co(III) ions partially oxidise or reduce to Co(III) and Co(II), respectively. The structure of the copper "components" in **1** bears structural features of monomeric copper units revealed in the tetrameric core of $[Cu(HTea)]_4 \cdot solv.$[10a] It can be suggested that coordinatively unsaturated copper aminoalkoxide generated *in situ* interacts as a ligand with the trinuclear "complex" $\{Co^{II}[Co^{III}(Tea)(O_2CMe)]_2\}$ to afford the pentanuclear mixed-metal compound **1**.

Magnetic properties

At room temperature the value of χT (4.1 emu K mol^{-1}) for **1** (Fig. 3) is in agreement with the presence of two uncorrelated $S = 1/2$ centres and one $S = 3/2$ centre with largely unquenched angular orbital momentum. On lowering the temperature, the value of χT slowly decreases: this may be attributed either to antiferromagnetic exchange coupling between Cu(II) and Co(II) or to the depopulation of the higher energy Kramers doublets of the Co(II) centres.[19]

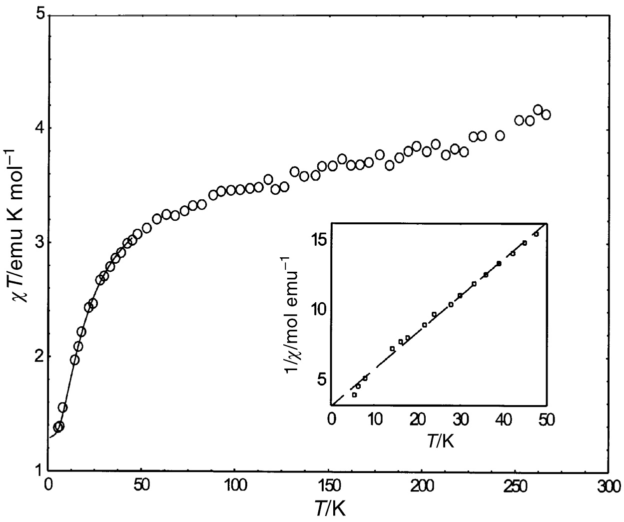


Fig. 3 χT *vs.* T curve for **1**. The continuous line is the fit obtained for the low T data using parameters reported in the text. The inset shows $1/\chi$ *vs.* T curve at low T, the dashed line being the Curie–Weiss plot obtained with parameters reported in the text.

It is generally accepted that the depopulation of the Kramers doublets originating from $^4T_{1g}$ is complete below 40 K.[20] Therefore, the observed decrease of χT below this temperature must be attributed to antiferromagnetic interactions between the metal centres. A Curie–Weiss plot was fitted with $\theta = 12.2$ K and $C = 3.8$ emu K mol^{-1} (5–50 K, inset of Fig. 3, dashed line). As the smallest contact between magnetic centres of different molecules is 7.181(3) Å, intermolecular interactions alone cannot account for the high value of θ for the Curie–Weiss fit. A fit was then attempted assuming an effective $S = 1/2$ ground state for Co(II) and an Ising-type anisotropy, considering only intramolecular interactions.[21,22] The spin Hamiltonian used was then: $\boldsymbol{H} = J_z(\boldsymbol{S}^z_{Cu1}\boldsymbol{S}^z_{Co} + \boldsymbol{S}^z_{Co}\boldsymbol{S}^z_{Cu2}) + (g_{Cu1} + g_{Co} + g_{Cu2})\mu_B B$, with $g_{x(Cu)} = g_{y(Cu)} = g_{z(Cu)}$ and assuming $g_{x(Co)} = g_{y(Co)} = 0$. With this formalism, positive J_z values mean an antiferromagnetic coupling. The parallel and perpendicular susceptibilities were calculated from the energy levels obtained by diagonalisation of the spin Hamiltonian for a magnetic field parallel and perpendicular to the z magnetic axis of our system. $\chi_\perp$ and $\chi_\parallel$ were then averaged to give the expression for the powder susceptibility:

$$\chi T = \frac{1}{3}\frac{N\beta^2}{k} \times \left\{ \frac{(g_{Cu} + \frac{1}{2}g_{zCo})^2 \exp(-J_z/kT) + (g_{Cu} - \frac{1}{2}g_{zCo})^2 \times \exp(J_z/kT) + \frac{1}{2}g^2_{zCo} + g^2_{Cu}(kT/J_z)\sinh(J_z/kT)}{2[1 + \cosh(J_z/kT)]} \right\} \tag{3}$$

The best fit (continuous line, Fig. 3) was obtained for $g_{zCo} = 10.4 \pm 0.1$, $g_{Cu} = 2.10 \pm 0.02$ and $J_z = 36 \pm 2$ cm^{-1}

$$\left(\text{with a residual sum, } s = \frac{\sum(\chi_o T - \chi_c T)^2}{n - 2} = 1.75 \times 10^{-3}\right).$$

While the value of g_{Cu} is in reasonable agreement with that obtained from the EPR spectra, the g_{zCo} value is higher than the value expected for high-spin Co(II) ($g_{Co} = 9$) and the obtained high value of J_z is unusual if one considers the structure of the system. This may, in principle, be justified by the very efficient role of the diamagnetic Co(III) in transmitting the interaction between Cu(II) and Co(II) at low temperature. A similar behaviour has been observed with exchange-coupled radicals interacting through the diamagnetic ion Ti(IV)[23] to give a fairly strong ferromagnetic coupling. However, from this analysis, a co-operative role of intra- and intermolecular interactions in determining the decrease of χT at low temperature cannot be excluded.

Conclusion

This paper describes a novel synthetic route to mixed-metal complexes developed using simple starting materials, relatively mild reaction conditions and the zerovalent metal in powdered form. The reaction for the formation of $[Cu^{II}_2Co^{II}Co^{III}_2(O_2CMe)_4(H_2Tea)_2(Tea)_2] \cdot 2(HO_2CMe)$ appears to be unprecedented, and the conventional synthesis using copper(II) and cobalt(II) salts in the presence of triethanolamine only yields a copper acetate complex with this ligand. Employing zerovalent metals in preparations of coordination compounds often leads to different reactivity than is found for the conventional synthesis and makes the study of such reactions extremely exciting. Investigations of novel chemical transformations involving zerovalent metals are of interest for an extensive range of problems and there will undoubtedly be increased activity in this area in the future.

Acknowledgements

The work was supported in part by the Fundamental Research State Fund of Ukraine and the Science and Technology Center in Ukraine (Project Gr-32j). NATO Expert Visit grant (HTECH.EV 972313, J. R.), the RSC Journals Grant for International Authors (V. N. K.) and the Royal Society Ex-quota Visits-FSU grant (O. Yu. V.) are gratefully acknowledged.

References

1 A. Bencini and D. Gatteschi, *Inorg. Chim. Acta*, 1978, **31**, 11.

2 See, for example: V. N. Kokozay and A. V. Sienkiewicz, *Polyhedron*, 1995, **14**, 1547; S. R. Petrusenko, V. N. Kokozay, O. Yu. Vassilyeva and B. W. Skelton, *J. Chem. Soc., Dalton Trans.*, 1997, 1793; K. V. Domasevitch, J. A. Rusanova, O. Yu. Vassilyeva, V. N. Kokozay, P. J. Squattrito, J. Sieler and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1999, 3087; V. V. Skopenko, V. N. Kokozay, O. Yu. Vassilyeva and V. A. Pavlenko, in *Direct Synthesis of Coordination and Organometallic Compounds*, ed. A. D. Garnovskii and B. I. Kharissov, Elsevier Science, Amsterdam, 1999, ch. 3, 5.

3 L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, J. Reedijk, B. W. Skelton and A. G. Oliver, *J. Chem. Soc., Dalton Trans.*, 1998, 2735; L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, B. W. Skelton and A. G. Oliver, *New J. Chem.*, 1998, **22**, 931 and references therein.

4 S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1993, 2875; N. Bricklebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1996, 157.

5 V. G. Kessler, L. G. Hubert-Pfalzgraf, S. Halut and J.-C. Daran, *J. Chem. Soc., Chem. Commun.*, 1994, 705.

6 V. V. Udovenko and V. N. Evreev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1963, **6**, 8.

7 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

8 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1993.

9 S. R. Hall, G. S. D. King and J. M. Stewart, *XTAL3.4. User's Manual*, University of Western Australia, Lamb, Perth, Australia, 1995.

10 (*a*) K. H. Whitmire, J. C. Hutchison, A. Gardberg and C. Edwards, *Inorg. Chim. Acta*, 1999, **294**, 153; (*b*) V. G. Makhankova, O. Yu. Vassilyeva, V. N. Kokozay, B. W. Skelton, G. A. Van Albada and J. Reedijk, *Polyhedron*, submitted.

11 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986, pp. 231–233; G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 251.

12 The Aldrich Library of FT-IR Spectra, Aldrich Chem. Co. Inc., USA, 1985.

13 (*a*) V. V. Udovenko, O. N. Stepanenko and B. G. Eroshok, *Zh. Neorg. Khim.*, 1974, **29**, 2455; L. G. Reyter, Yu. I. Pavlenko and O. A. Tarasenko, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1997, **63**, 106; (*b*) V. N. Evreev and S. V. Murashko, *Zh. Neorg. Khim.*, 1974, **29**, 2448.

14 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.

15 A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.

16 (*a*) F. P. W. Agterberg, H. A. J. Provó Kluit, W. L. Driessen, H. Oevering, W. Buijs, M. T. Lakin, A. L. Spek and J. Reedijk, *Inorg. Chem.*, 1997, **36**, 4321; (*b*) F. P. W. Agterberg, H. A. J. Provó Kluit, W. L. Driessen, J. Reedijk, H. Oevering, W. Buijs, N. Veldman, M. T. Lakin and A. L. Spek, *Inorg. Chim. Acta*, 1998, **267**, 183; (*c*) G. A. van Albada, J. G. Haasnoot, J. Reedijk, M. Biagini-Cingi, A. M. Manotti-Lanfredi and F. Ugozzoli, *Polyhedron*, 1995, **14**, 17.

17 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Clarendon Press, Oxford, 1986.

18 (*a*) T. Sh. Kapanadze, Yu. E. Gorbunova, Yu. V. Kokunov and Yu. A. Buslaev, *Mendeleev Commun.*, 1991, 55; (*b*) J. A. Bertrand, J. A. Kelley and E. G. Vassian, *J. Am. Chem. Soc.*, 1969, **91**, 2394; (*c*) A. Golobic, B. Štefane and S. Polanc, *Polyhedron*, 1999, **18**, 3661.

19 L. Banci, A. Bencini, C. Benelli, D. Gatteschi and C. Zanchini, *Structure Bonding* (*Berlin*), 1982, **52**, 37.

20 P. J. Van Koningsbruggen, J. G. Haasnoot, W. Vreugdenhil, J. Reedijk and O. Kahn, *Inorg. Chim. Acta*, 1995, **239**, 5.

21 O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993; R. L. Carlin, *Magnetochemistry*, Springer Verlag, Berlin, 1986.

22 E. Coronado, M. Drillon, P. R. Nutgeren, L. J. De Jongh and D. Beltran, *J. Am. Chem. Soc.*, 1988, **110**, 3907.

23 A. Caneschi, A. Dei and D. Gatteschi, *J. Chem. Soc., Chem. Commun.*, 1992, 630.