# Formation, Structures, and Magnetic and EPR Spectroscopic Properties of Dicobalt(III)-Dicopper(II) Complexes Featuring Heterotetranuclear Cations of a Puckered Cyclic Structure with Diethanolamine and Diethanolamine(2−) as Bridging Ligands

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The compounds $[Cu^{II}_2Co^{III}_2(H_2dea)_2(dea)_4]X_2(Solv)_n$ [X = Cl (**1**), Br (**2**), SCN (**3**), $O_2CMe$ (**4**), I (**5**); Solv = $H_2O$ or/and $CH_3OH$, DMF, $n$ = 1–4] were synthesised by the reaction of zero-valent copper with cobalt(II) salts in non-aqueous ($CH_3OH$, DMF, DMSO) solutions of diethanolamine ($H_2dea$) in air. Crystallographic investigations of **1**–**4** reveal that the complexes contain the centrosymmetric cation $[Cu_2Co_2(H_2dea)_2(dea)_4]^{2+}$ in which the four metal atoms are linked together by bridging oxygen atoms of the six ligand groups to form a parallelogram with the length of the short edge (Cu···Co) being ca. 2.83 Å and a short diagonal distance (Cu···Cu) at approximately 3.23–3.29 Å. The copper atom is five-coordinate with a square-pyramidal geometry; the geometry at the trivalent cobalt ion is almost octahedral. The tetranuclear units are further stabilized by intramolecular O–H···O and N–H···O hydrogen bonds. The hydrogen-bonded network that involves the OH and NH groups of the ligands, uncoordinated anions, and solvent molecules links the tetranuclear units together and results in the formation of extended two- and three-dimensional networks. Variable-temperature magnetic susceptibility measurements of **1**–**3** and **5** show no significant exchange coupling between the copper centres. The frozen-solution and solid-state EPR spectra at 77 K are characteristic of a triplet state with the hyperfine structure distinctly resolved in solution. On the assumption of noncoaxiality of the $g$ and $D$ tensors the spectra were interpreted with the zero-field-splitting parameters $D$ = 0.0560(1) (**2**–**5**) and $D$ = 0.0712(1), $E$= 0.0028(2) cm$^{-1}$ (**1**). Dominant contributions to the observed EPR zero-field splitting are presumed to be dipole-dipole in origin.

## Introduction

The development of new approaches to the preparation of mixed-metal complexes plays an important role in synthetic coordination chemistry. Our current research in this field has been focused on the synthesis of Cu/M (M = Co,[1] Zn,[2] Ni) compounds. Investigation of their physico-chemical and catalytic properties may elucidate features found in polynuclear biologically active molecules, in which copper ions play an essential role in processes such as electron transfer, oxidation and dioxygen transport.[3]

A convenient synthetic pathway to such complexes has proven to be the use of zero-valent copper, a metal salt, and an amino alcohol as starting materials in solution in air. As we showed earlier, metal powders ($Cu^0$, $Ni^0$, $Zn^0$) dissolved to form metal complexes in the presence of an ammonium salt (a proton donating agent) and dioxygen from the air via Equation (1)

$$M^0 + 2\,NH_4^+ + 1/2\,O_2 \rightarrow M^{2+} + H_2O + NH_3 \qquad (1)$$

in which copper oxidation occurs in the two-step process $Cu \rightarrow Cu^+ \rightarrow Cu^{2+}$.[4] The concept of the need for a proton-donating agent in syntheses of coordination compounds from elemental metals in air was further developed into a methodology for the preparation of mixed-metal complexes.[5] We believed that coordinatively unsaturated copper aminoalkoxides generated in situ could easily interact with other metal ions present in solution to afford the formation of a mixed-metal compound, due to the estab-

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lished ability of amino alcohols to form polynuclear metal complexes.[6]

A unique pentanuclear mixed-valence complex[1a] $[Cu^{II}_2Co^{II}Co^{III}_2(O_2CMe)_4(H_2tea)_2(tea)_2]\cdot 2(HO_2CMe)$ was obtained by the reaction of copper powder with cobalt(II) acetate and triethanolamine ($H_3tea$) in DMF solution in air. A marked decrease of the $\chi T$ value below 40 K for this compound was attributed to antiferromagnetic exchange coupling between the $Cu^{II}$ and $Co^{II}$ magnetic centres interacting through the diamagnetic $Co^{III}$ ions. We therefore started systematic investigations into the reactions of zerovalent copper and a cobalt(II) salt in the presence of another amino alcohol, diethanolamine [$H_2dea$, $NH(C_2H_4OH)_2$], and wish to report here the synthesis, crystal structures, spectroscopic investigations and magnetochemistry of the compounds $[Cu^{II}_2Co^{III}_2(H_2dea)_2(dea)_4]X_2(Solv)_n$ [X = Cl (**1**), Br (**2**), SCN (**3**), $O_2CMe$ (**4**), I (**5**); Solv = $H_2O$ or/and $CH_3OH$, DMF, $n = 1-4$].

## Results and Discussion

### Synthesis

When copper powder and cobalt(II) salts (chloride, bromide, iodide, thiocyanate, or acetate) were treated with nonaqueous ($CH_3OH$, DMF, DMSO) solutions of diethanolamine in air, dissolution of copper occurred within several hours whilst stirring at 50−60 °C, resulting in the formation of dark green solutions. These solutions slowly precipitated green crystalline products that were isolated as the corresponding solvates or hydrates in high yields. Crystals of an iodide complex formed in methanol appeared to lose solvent and crystallinity within minutes if left to stand exposed to a solvent-free atmosphere. The compounds showed analytical data accounting for the presence of $Cu^{II}$ and $Co^{III}$ in a 1:1 stoichiometry. Their formation can be understood if one considers the reaction scheme in Equation (2).

$$\begin{aligned}&2\,Cu^0 + 2\,CoX_2 + 8\,H_2dea + 1.5\,O_2 + n\,Solv \rightarrow\\&[Cu^{II}_2Co^{III}_2(H_2dea)_2(dea)_4]X_2\cdot n\,Solv + 2\,H_2dea\cdot HX + 3\,H_2O\end{aligned} \qquad (2)$$

The assumption of neutral and doubly deprotonated amino alcohols that follows from counting the electrostatic charges was verified structurally. A similar tetranuclear cation was found for the mixed-valence dark green cobalt complex $[Co^{II}_2Co^{III}_2(H_2dea)_2(dea)_4](ClO_4)_2$ (**6**),[7] prepared from a $Co^{II}$ salt in air. This observation suggests that the structure and nuclearity of these complexes are governed by the ligand nature of diethanolamine in its interaction with $Co^{II}$ ions in solution. The presence of the amino alcohol facilitates partial air oxidation of the initial $Co^{II}$ to $Co^{III}$ in the case of **6**. When metallic copper is involved the formation of a mixed-metal complex becomes more favourable and all the initial $Co^{II}$ ions oxidise to $Co^{III}$.

### Spectroscopic Characterization

The IR spectra of complexes **1**−**5** in the range 4000−400 $cm^{-1}$ are quite similar, and show all the characteristic ligand peaks. The spectra indicate the presence of hydrogen-bonded (3300−3400 $cm^{-1}$) OH groups only; free (≈ 3600 $cm^{-1}$) OH groups are not observed.[8] Compound **3** shows the sharp, intense ν(CN) absorption at 2090 $cm^{-1}$ and a weak band for ν(CS) of a thiocyanate group at 745 $cm^{-1}$. The δ(NCS) mode is obscured by other vibrations. The frequencies of the observed bands suggest a terminal N-bonded thiocyanate,[9] although this is not supported by the X-ray structural study (vide infra). Participation of the uncoordinated $NCS^-$ group in the intermolecular hydrogen bonding may account for this observation (the $N_{NCS}\cdots O_{solvent}$ contacts of about 2.8 Å support such hydrogen bonding).

The IR spectrum of **4** displays two bands at 1600 and 1380 $cm^{-1}$ of higher and lower intensity ($\Delta = 220$ $cm^{-1}$), respectively, not observed in the spectra of **1**−**3** and **5** and therefore assigned to $\nu(CO_2)$ vibrations. The Δ values above 200 $cm^{-1}$ for the acetato complexes appear generally to be associated with unidentate coordination.[8,10] This criterion is not applicable to **4**, as the results of the X-ray structural study show that the acetate oxygen atoms are not coordinated to metals. However, those oxygens are strongly hydrogen bonded to methanol and the NH groups of the amino alcohol, giving what may be regarded as a "pseudo-bridging" arrangement responsible for the observed spectral pattern. Also, the possibility of anion exchange in a KBr disc and pressure-induced changes cannot be ruled out in the case of **3** and **4**.

The absorption spectra of **1**−**5** in DMF are dominated by the low-energy broad absorption at approximately 600 nm, attributable to a superposition of transitions in the visible region of a low-spin cobalt(III) ion in an octahedral geometry and a five-coordinate copper(II) centre, as revealed in the crystal structure.[11] The high energy, very intense band lower than 330 nm is associated with a charge-transfer transition.

### Molecular and Crystal Structures of 1−4

All four complexes consist of the tetranuclear cation $[Cu_2Co_2(H_2dea)_2(dea)_4]^{2+}$, which has a puckered cyclic structure, two anions, and several solvent molecules in the crystal lattice. The overall structural configurations of the cation for **1**−**4** are similar. The important differences show up as relatively small changes in bond lengths and angles (Table 1) as well as in the hydrogen bonding. The molecular diagram and numbering scheme of **1** is shown in Figure 1, which illustrates the general geometry of the compounds.

The existence of an inversion centre induces all metal centres to lie in the same plane. The four metal atoms are linked together by the bridging oxygen atoms of the six diethanolamine groups to form a parallelogram with the length of the short edge [Cu(1)−Co(2)] being ca. 2.83 Å and a short diagonal distance [Cu(1)−Cu(1′)] at approximately 3.23−3.29 Å (Table 1). Our assignments of the positions of the metal ions are based on the relative metal−N(O) bond lengths and the geometric features of the two chromophores. The atom Cu(1) is five-coordinate with a square-pyramidal geometry. The four copper-ligand

Table 1. Selected bond lengths (Å) and angles (°) for **1−4**[a]

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Cu(1)−O(1′) | 1.945(1) | 1.941(6) | 1.94(2) | 1.9453(7) |
| Cu(1)−O(3) | 1.981(1) | 1.978(6) | 1.96(2) | 1.9547(7) |
| Cu(1)−O(5) | 2.356(2) | 2.352(11) | 2.37(2) | 2.408(1) |
| Cu(1)−O(4) | 1.974(1) | 1.966(7) | 1.93(2) | 1.9843(6) |
| Cu(1)−N(3) | 2.029(1) | 2.017(9) | 2.00(2) | 2.0151(7) |
| Co(2)−O(2) | 1.893(1) | 1.885(8) | 1.92(1) | 1.9061(7) |
| Co(2)−O(4) | 1.904(1) | 1.901(7) | 1.91(2) | 1.9116(8) |
| Co(2)−N(2) | 1.939(2) | 1.924(11) | 1.91(3) | 1.952(1) |
| Co(2)−O(1) | 1.904(1) | 1.895(9) | 1.89(2) | 1.9074(8) |
| Co(2)−O(3) | 1.926(1) | 1.915(8) | 1.91(2) | 1.9116(7) |
| Co(2)−N(1) | 1.955(2) | 1.950(9) | 1.96(3) | 1.949(1) |
| Cu(1)···Co(2) | 2.8445(3) | 2.818(2) | 2.820(6) | 2.8294(2) |
| Cu(1)···Cu(1′) | 3.2955(4) | 3.261(3) | 3.237(6) | 3.2308(2) |
| O(1′)−Cu(1)−O(4) | 92.99(5) | 93.3(3) | 94.7(7) | 94.86(3) |
| O(4)−Cu(1)−O(3) | 82.12(5) | 82.2(3) | 82.7(7) | 81.98(3) |
| O(4)−Cu(1)−N(3) | 177.90(7) | 177.8(4) | 177.4(9) | 176.78(5) |
| O(1′)−Cu(1)−O(5) | 92.42(5) | 93.4(3) | 91.3(8) | 90.69(3) |
| O(3)−Cu(1)−O(5) | 105.06(5) | 104.7(3) | 106.1(8) | 106.83(3) |
| O(1′)−Cu(1)−O(3) | 162.48(6) | 161.9(4) | 162.6(8) | 162.47(4) |
| O(1′)−Cu(1)−N(3) | 86.53(5) | 87.3(3) | 85.4(8) | 86.58(3) |
| O(3)−Cu(1)−N(3) | 97.73(5) | 96.6(3) | 96.5(8) | 95.78(3) |
| O(4)−Cu(1)−O(5) | 102.67(5) | 101.9(3) | 103.8(8) | 101.56(3) |
| N(3)−Cu(1)−O(5) | 79.40(6) | 80.2(4) | 78.7(8) | 81.27(4) |
| O(2)−Co(2)−O(1) | 92.11(5) | 92.7(4) | 91.9(7) | 91.83(3) |
| O(1)−Co(2)−O(4) | 89.29(6) | 89.0(3) | 90.1(8) | 90.27(3) |
| O(1)−Co(2)−O(3) | 91.86(5) | 90.5(4) | 91.0(8) | 89.66(3) |
| O(2)−Co(2)−N(2) | 91.67(6) | 93.0(4) | 90.0(9) | 91.84(4) |
| O(4)−Co(2)−N(2) | 87.43(6) | 87.1(4) | 87.0(1) | 84.83(4) |
| O(2)−Co(2)−N(1) | 86.74(5) | 87.0(4) | 87.9(8) | 86.85(3) |
| O(4)−Co(2)−N(1) | 174.36(7) | 174.8(4) | 176(1) | 175.56(4) |
| N(2)−Co(2)−N(1) | 98.21(7) | 98.1(4) | 97.0(1) | 99.60(4) |
| O(2)−Co(2)−O(4) | 93.03(5) | 92.0(3) | 93.3(7) | 93.21(3) |
| O(2)−Co(2)−O(3) | 175.72(6) | 176.0(4) | 176.4(9) | 177.71(5) |
| O(4)−Co(2)−O(3) | 85.44(5) | 85.6(3) | 84.6(7) | 85.04(3) |
| O(1)−Co(2)−N(2) | 175.12(5) | 173.2(4) | 176(1) | 174.04(4) |
| O(3)−Co(2)−N(2) | 84.28(6) | 83.7(4) | 87.0(9) | 86.54(3) |
| O(1)−Co(2)−N(1) | 85.09(6) | 85.9(4) | 86.0(1) | 85.29(4) |
| O(3)−Co(2)−N(1) | 95.18(5) | 95.7(4) | 94.5(8) | 95.01(4) |

[a] Symmetry transformations used to generate equivalent atoms (indicated by ′): 1 − *x*, 1 − *y*, 1 − *z*.

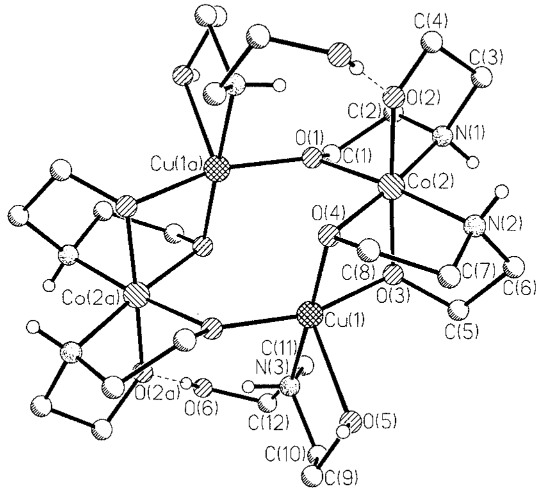

Figure 1. Molecular structure of the tetranuclear cation of **1**

bonds in the plane have normal bond lengths (average Cu−O and Cu−N distances of 1.96 and 2.02 Å, respectively), while the axial Cu−O(5) bond is elongated [2.352(11)−2.408(1) Å] due to the Jahn−Teller effect in the $d^9$ electronic configuration (Table 1). This long distance also allows one to infer the existence of the hydroxo donor function of the O(5) oxygen atom. The geometry at the trivalent cobalt ion, Co(2), is almost octahedral with Co(2)−O(N) distances in the range 1.885(8)−1.955(2) Å (Table 1), similar to those of low-spin cobalt(III) in an octahedral environment.[12] The structure of the tetranuclear cation is similar to that found for the mixed-valence cobalt complex **6**[7] in which the positions of the $Co^{II}$ ions correspond to those of $Cu^{II}$ in **1−4**.

The uncoordinated ethanol group of the neutral diethanolamine ligand forms an intramolecular hydrogen bond with the ethanolato group of the $dea^{2-}$ ligand, as evidenced by the O(6)···O(2′) distances and O−H···O angles (Table 2, Figure 1). There is also a weaker intramolecular H bond between N(3) and O(2′) atoms (Table 2).

Table 2. Parameters of the intramolecular H-bonding for **1−4**, bond lengths (Å) and angles (°)[a]

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| H(6O)−O(2′) | 1.87(3) | 1.35 | | 1.97(2) |
| O(6)···O(2′) | 2.592(2) | 2.60(1) | 2.62 | 2.731(1) |
| O(6)−H(6O)−O(2′) | 178(4) | 168 | | 172(3) |
| H(3N)···O(2′) | 2.12(2) | 1.93 | 2.00 | 2.06(2) |
| N(3)···O(2′) | 2.931(2) | 2.90(1) | 2.88(3) | 2.911(1) |
| N(3)−H(3N)−O(2′) | 163(3) | 164 | 158 | 170(2) |

[a] Symmetry transformations used to generate equivalent atoms (indicated by ′): −*x* + 1, −*y* + 1, −*z* + 1.

Intermolecular hydrogen bonding involving the OH and NH groups of the ligands, the uncoordinated anions, and solvent molecules, links the tetranuclear units together and results in the formation of extended two- and three-dimensional networks. A fragment of the solid-state structure of **4** is given in Figure 2 as a representative example. We believe that the participation of solvent molecules in the hydrogen-bonded network is essential for the complex integrity in the solid state.

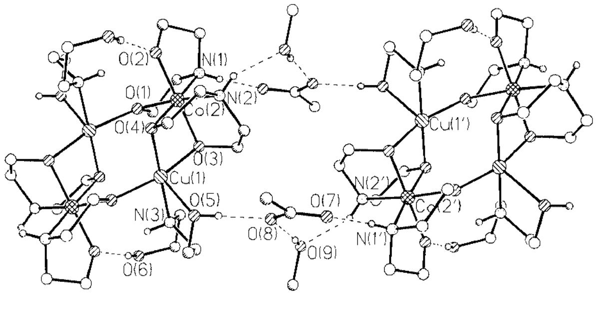

Figure 2. View of **4** showing the hydrogen-bonded network involving the noncoordinating acetate groups and methanol molecules

All bond lengths and angles within neutral and deprotonated diethanolamine are normal, and these data are given as supplementary material. Thiocyanate [$d$(N−C) 1.14(6), $d$(S−C) 1.59(4) Å, ∠N−C−S 170(4)°] and acetate groups [$d$(O−C) ca. 1.256(2), $d$(C−C) 1.519(2) Å, ∠ O−C−O 124.9(1), ∠C−C−O 117.5(1)°] are structurally normal.[12]

### Magnetic Properties

Experimental magnetic data for **1**−**3** and **5** are displayed in Figure 3 as $\mu_{eff}$ vs. $T$ plots. The experimental data are presented as solid lines to distinguish between different plots. These show that in all cases the magnetic behaviour is paramagnetic. On the assumption that the Co$^{III}$ ions are diamagnetic, the room temperature magnetic moment for each copper atom, ca. 1.8−1.9 B.M., is in the normal range for isolated $S$ = 1/2 ions. The drop in the effective magnetic moment below 6 K indicates the onset of a weak antiferromagnetic coupling; this is not unexpected for systems in which H-bond contacts are important. It can be concluded that -O−Co−O- bridges effectively prevent any exchange interactions between copper centres.

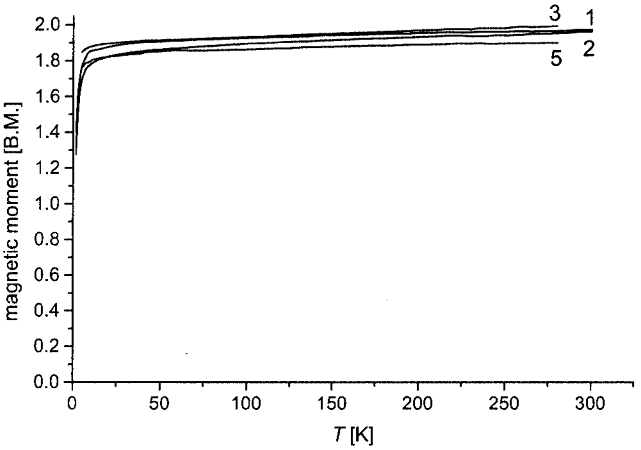

Figure 3. Plots of the effective magnetic moment per copper atom vs. $T$ for **1**−**3** and **5**

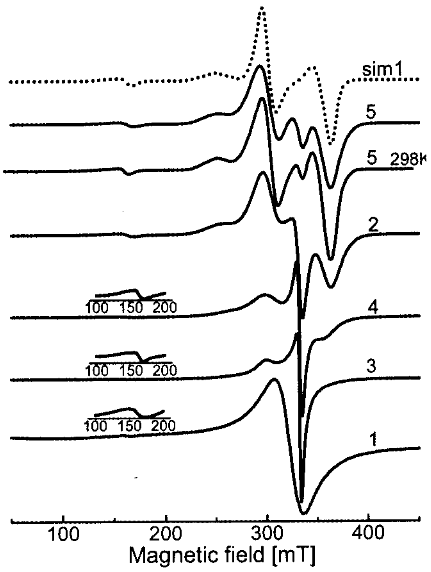

Figure 4. EPR spectra of polycrystalline complexes **1**−**5** measured at 77 K (solid lines), the dotted line being the simulated (sim1) spectrum obtained with parameters reported in the text

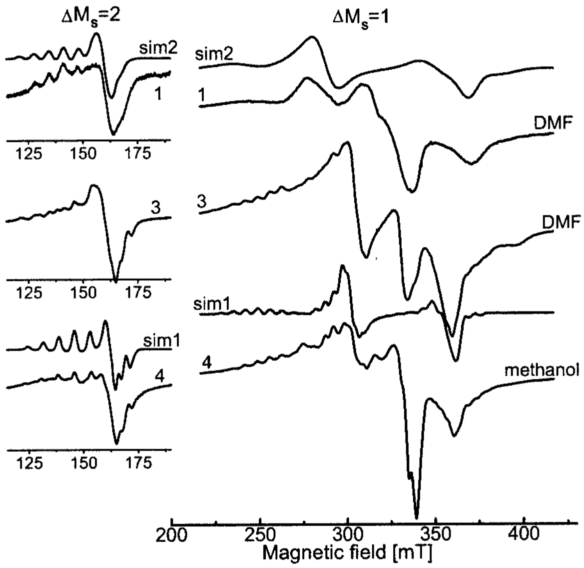

Figure 5. EPR spectra of frozen solutions of **1** and **3** in DMF and **4** in methanol (77 K); sim1 and sim2 are the fits obtained for the frozen solution spectra for **2**−**5** in DMF and methanol and for **1** in DMF, respectively, using parameters reported in the text

The polycrystalline powder EPR spectra of **1**−**5** (Figure 4), which are essentially similar, show characteristic features of the spin-triplet state with the half-field signal observed (ca. 160 mT).[13] Fine structure components due to $\Delta M_S$ = 1 transitions are distinctly visible for compounds **2** and **5**, and partly for **3** and **4**. In the case of compound **1** the $\Delta M_S$ = 1 triplet-state components are not resolved. The spectra contain an isotropic signal in the $g \approx 2$ region, indicating crystal defects or monomeric impurities of different contribution. No sharpening of the lines or hyperfine splitting was observed upon cooling from room temperature to 77 K.

Nicely resolved spectra of the complexes showing almost identical triplet-state patterns were obtained from fresh solutions in DMF and methanol (77 K) (see Figure 5 for a representative example). The hyperfine structure from the two coupled Cu$^{II}$ centres is clearly observed for the $\Delta M_S$ = 1 and $\Delta M_S$ = 2 signals and also partly resolved on the line present in frozen solution spectra only at ca. 375 mT, which is attributed to a high-field "parallel" line (Figure 5). Careful examination of the $\Delta M_S$ = 2 signals (using the accumulation procedure) reveals two sets of "parallel" orientation lines for compounds **3** and **5** in DMF (Figure 5). One of them corresponds to that observed for all other compounds; the second is most likely associated with the additional spin-triplet line seen at 397 mT for **3** and **5** in DMF, suggesting a very small contribution of other triplet-state species.

No substantial variation of the zero-field splitting for the different complexes was observed in both DMF and methanol frozen solutions, except compound **1**. However, the relative intensities of the fine-structure signals and signals due to paramagnetic species vary for the two solvents. The former signals are much more intense in DMF, indicating that tetranuclear $[Cu_2Co_2(H_2dea)_2(dea)_4]^{2+}$ cations are destroyed by the alcohol to a greater extent. The triplet-state spectra became weaker with time and the paramagnetic species contribution substantially increased.

The triplet EPR spectra are described by the spin Hamiltonian shown in Equation (3):[14]

$$H = \mu_B B\{g\}\,S + I\{A\}S + D[S_z^2 - 1/3\,S(S+1)] + E(S_x^2 - S^2_y) \quad (3)$$

The experimental spectra have been fitted with nonparallel *g* and *D* tensors through a computer simulation procedure as described in refs.[15–17] The main features of the solid-state and frozen solution (methanol, DMF) spectra of compounds **2–5** were well simulated with the same set of spin-Hamiltonian parameters ("sim1" in Figure 4 and 5), $g_z = 2.305(5)$, $g_x = 2.063(2)$, $g_y = 2.063(2)$, $A_z = 0.0070(2)$, $A_x = 0.0014(4)$, $A_y = 0.0010(4)$ cm$^{-1}$, $D = 0.0560(1)$ cm$^{-1}$ and an angle (α) between $g_{zz}$ and $D_{zz}$ directions of 25(1)°. In the polycrystalline powder spectrum of **1** the high intensity of the isotropic signal and the low resolution of the triplet signals make a determination of the *g* and *D* values impossible. Dissolution of the compound in DMF afforded the triplet-state spectrum (77 K) with the following spin-Hamiltonian parameters ("sim2" in Figure 5): $g_z = 2.350(5)$, $g_x = 2.068(2)$, $g_y = 2.068(2)$, $A_z = 0.0070(2)$, $A_x = 0.0012(4)$, $A_y = 0.0012(4)$ cm$^{-1}$, $D = 0.0712(1)$ cm$^{-1}$, $E = 0.0028(2)$ cm$^{-1}$, α = 30(1)°.

These results clearly indicate that the configuration of the tetranuclear cations is retained in solution. Since no significant exchange coupling between copper centres is involved, according to the solid-state magnetic susceptibility studies for the reported compounds, the dominant interaction that brings about the characteristic shape of the EPR spectra is presumed to be dipole-dipole in origin.[13] Assuming only dipolar contributions to the observed EPR zero-field splitting, the empirical formula[18] would yield a separation of 3.4 (**2–5**) and 3.2 Å (**1**) for the Cu–Cu distance, which are in nice — although not very accurate — agreement with the solid-state distances (Table 1). The following observation also provides support for such a conclusion. In the case of dominant dipolar effects, the largest component of the zero-field-splitting tensor, $D_{zz}$, is parallel to the Cu–Cu direction; the largest *g* value for a square pyramidal copper(II) is expected to be orthogonal to the plane of equatorial ligands.[19] According to the crystallographic studies of compounds **1–4** the normal to the least-squares plane provided by N(3), O(3), O(4), and O(1′) makes an angle of ca. 30° with the axis joining the two copper centres. The value obtained is in good agreement with the values of α derived from the assumption of the noncoaxiality of the *g* and *D* tensors.

## Concluding Remarks

Once again, employing zero-valent metals as a source of one of the metals in the synthesis of mixed-metal compounds allowed the generation of remarkable crystal structures, such as the heterotetranuclear dicobalt(III)dicopper(II) complexes containing diethanolamine.

Magnetic susceptibility measurements and EPR triplet spectra of the complexes showed evidence that the zero-field splitting parameter *D* originates from dipole-dipole interactions. The structure of the tetranuclear cations is fully preserved in solution and magnetic dipole-dipole coupling between the copper(II) ions is maintained.

## Experimental Section

**General:** All chemicals were of reagent grade, and were used as received. All experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy, and potentiometric titration with a solution of $K_3[Fe(CN)_6]$ for Co$^{II}$,[20] using standard titrimetric methods for anions and a Carlo Erba Strumentazion Analyzer (for C, H and N). Infrared spectra were recorded as KBr discs or as Nujol mulls on a UR-10 spectrophotometer in the 4000–400 cm$^{-1}$ region using conventional techniques. UV/Vis DMF solution spectra were recorded on a Perkin–Elmer Lambda 12 spectrometer. The EPR spectra were recorded on a Bruker ESP 300E (Bruker, Germany) spectrometer operating at X-band and equipped with a Bruker NMR gaussmeter ER 035M and a Hewlett–Packard microwave frequency counter HP 5350B. Variable-temperature magnetic measurements on complexes **1** and **2** in the region 1.8–300 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in capsules. Magnetic susceptibility measurements for compounds **3** and **5** were recorded 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. In all cases, diamagnetic corrections for the sample holders were applied to the data. Diamagnetic corrections for the samples were determined from Pascal's constants.[21]

**General Procedure for the Synthesis of 1–5:** Copper powder (0.32 g, 5 mmol), $Co(X)_2{\cdot}nH_2O$ (5 mmol) (X = Cl, Br, I, NCS, $O_2CMe$; *n* = 1–6), $CH_3OH$ (10 cm$^3$, DMF in the case of **5**) and $H_2dea$ (4 cm$^3$) were heated to 50–60 °C and stirred magnetically until total dissolution of Cu was observed (several hours). The resulting solutions were allowed to stand at room temperature for one week during which time dark-green crystalline products of **1–5** precipitated. They were filtered off, washed with dry 2-propanol and finally dried in vacuo at room temperature.

**$[Cu_2Co_2(H_2dea)_2(dea)_4]Cl_2{\cdot}2H_2O$ (1):** Mass collected: 1.36 g, yield 56%. IR (KBr): ṽ = 3370 br, 3145 s, 3105 s, 2970 sh, 2940 m, 2900 m, 2885 m, 2860 m, 1660 br, 1450 m, 1375 w, 1350 sh, 1340 w, 1270 w, 1250 w, 1235w, 1220 w, 1185 w, 1165 w, 1115 sh, 1105 s, 1080 m, 1060 vs, 1040 sh, 1020 sh, 925 w, 915 w, 900 w, 880 w, 865 w, 830 w, 680 w, 645 m, 600 w, 570 sh, 560 m, 535 m, 500 w, 480 w, 445 w. $C_{24}H_{62}Cl_2Co_2Cu_2N_6O_{14}$ (974.65): calcd. Cu 13.04, Co 12.09, Cl 7.27, C 29.58, H 6.41, N 8.62; found Cu 13.4, Co 12.0, Cl 7.6, C 28.8, H 6.6, N 8.1.

**$[Cu_2Co_2(H_2dea)_2(dea)_4]Br_2{\cdot}2H_2O{\cdot}2CH_3OH$ (2):** Mass collected: 1.20 g, yield 43%. IR (KBr): ṽ = 3400 br, 3160 s, 3115 s, 2940 m, 2890 w, 2880 m, 2850 m, 1650 br, 1450 m, 1375 w, 1350 sh, 1340 w, 1270 w, 1250 w, 1235 w, 1215 w, 1180 w, 1150 w, 1110 sh, 1100 s, 1080 m, 1055 vs, 1040 sh, 1020 sh, 925 w, 915 w, 900 w, 880 w, 865 w, 825 w, 720 w, 680 w, 645 m, 595 w, 570 sh, 560 m, 535 m, 495 w, 480 w, 445 w cm$^{-1}$. $C_{26}H_{70}Br_2Co_2Cu_2N_6O_{16}$, (1127.64): calcd. Cu 11.27, Co 10.45, Br 14.17, C 27.69, H 6.26, N 7.45; found Cu 11.8, Co 10.9, Br 14.6, C 27.8, H 6.3, N 7.8.

**$[Cu_2Co_2(H_2dea)_2(dea)_4](NCS)_2$·2CH$_3$OH (3):** Mass collected: 0.73 g, yield 28%. IR (KBr): $\tilde{\nu}$ = 3400 br, 3300−3100 br, 2935 m, 2870 m, 2830 sh, 2090 s, 1630 br, 1450 m, 1425 m, 1380 w, 1365 w, 1270 w, 1250 w, 1215 w, 1155 w, 1120 sh, 1095 m, 1060 vs, 1045 vs, 1015 sh, 920 w, 915 w, 885 w, 860 w, 830 w, 745 w, 665 w, 645 m, 595 w, 570 w, 555 m, 520 m, 500 w, 480 w, 465 w cm$^{-1}$. $C_{28}H_{66}Co_2Cu_2N_8O_{14}S_2$ (1047.95): calcd. Cu 12.13, Co 11.25, NCS 11.08, C 32.09, H 6.35, N 11.36; found Cu 12.7, Co 11.6, NCS 11.0, C 31.2, H 6.1, N 10.7.

**$[Cu_2Co_2(H_2dea)_2(dea)_4](O_2CMe)_2$·2CH$_3$OH (4):** Mass collected: 1.25 g, yield 48%. IR (KBr): $\tilde{\nu}$ = 3430 br, 3220−3100 br, 2935 m, 2870 m, 2830 m, 1600 s, 1435 m, 1390 sh, 1380 m, 1330 m, 1275 w, 1250 w, 1220 w, 1180 w, 1120 w, 1100 m, 1055 vs, 1035 sh, 1020 sh, 920 w, 915 sh, 890 w, 880 w, 860 w, 820 w, 675 w, 645 m, 615 w, 600 w, 590 w, 570 m, 555 m, 520 m, 500 w, 480 w, 465 w cm$^{-1}$. $C_{30}H_{72}Co_2Cu_2N_6O_{18}$ (1049.89): calcd. Cu 12.11, Co 11.23, C 34.32, H 6.91, N 8.00; found Cu 12.3, Co 11.4, C 33.5, H 7.0, N 7.9.

**$[Cu_2Co_2(H_2dea)_2(dea)_4]I_2$·2DMF (5):** Mass collected: 1.53 g, yield 48%. IR (KBr): $\tilde{\nu}$ = 3450 br, 3300−3050 br, 2935 m, 2875 m, 2835 sh, 1660 s, 1440 m, 1400 m, 1370 w, 1350 w, 1250 w, 1185 w, 1160 w, 1110 sh, 1100 m, 1060 vs, 1030 sh, 1020 sh, 920 w, 900 w, 880 w, 855 sh, 830 w, 675 w, 645 m, 600 w, 570 m, 555 m, 525 m, 500 m, 480 w, 450 w cm$^{-1}$. $C_{30}H_{72}Co_2Cu_2I_2N_8O_{14}$ (1267.73): calcd. Cu 10.03, Co 9.30, I 20.02, C 28.42, H 5.72, N 8.84; found Cu 9.9, Co 9.0, I 20.3, C 29.2, H 5.9, N 8.8.

**X-ray Crystallographic Investigations:** Diffraction experiments were performed on a Bruker SMART CCD diffractometer (ω rotation scans with narrow frames) (**1**, **4**) and an Enraf−Nonius CAD-4 diffractometer operating in the ω/2θ scan mode (**2**, **3**) equipped with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) (**1**, **2**, **4**) and Cu-$K_\alpha$ radiation ($\lambda$ = 1.54178 Å) (**3**). The data were corrected for Lorentz polarisation effects and for the effects of absorption [multi-scan (**1**, **4**), Gaussian (**2**, **3**)]. The structures were solved by direct methods using the XTAL3.5[22] (**1**, **4**) and SHELXS-86[23] (**2**, **3**) programs, and refined by full-matrix least-squares methods on *F* using SHELXL-93[24] and XTAL3.5.[22] Details of the structural investigations and crystallographic data are summarized in Table 3.

In most cases (**1**, **2**, **4**), the non-hydrogen atoms were refined anisotropically (full-matrix least-squares). For both **1** and **4** all hydrogen atoms were located in a difference Fourier synthesis and refined isotropically. For **2** hydrogen atoms were included in their calculated positions, except hydroxyl hydrogen atoms, which were located but not refined. The ethanol solvent OH hydrogen atom was not located. For **3**, carbon atoms were refined with isotropic displacement parameters. The solvent methanol was refined with two disordered components with site occupancy factors set at 0.75 and 0.25 after initial trial refinement. Hydrogen atoms were included in

Table 3. Crystallographic data and relevant data referring to the structure solution and refinement

| Compound | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Empirical Formula | $C_{24}H_{62}Cl_2Co_2Cu_2N_6O_{14}$ | $C_{26}H_{70}Br_2Co_2Cu_2N_6O_{16}$ | $C_{28}H_{66}Co_2Cu_2N_8O_{14}S_2$ | $C_{30}H_{72}Co_2Cu_2N_6O_{18}$ |
| Molecular mass | 974.65 | 1127.64 | 1047.97 | 1049.89 |
| Cryst. size [mm] | 0.5 × 0.28 × 0.24 | 0.25 × 0.45 × 0.45 | 0.40 × 0.29 × 0.27 | 0.4 × 0.4 × 0.15 |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| CCDC deposit no. | 164276 | 164275 | 164274 | 164273 |
| *a* [ Å] | 11.338(1) | 10.092(2) | 11.048(2) | 8.4439(5) |
| *b* [ Å] | 17.831(2) | 10.749(2) | 15.913(3) | 11.4758(7) |
| *c* [ Å] | 10.229(1) | 11.477(2) | 13.023(3) | 11.9843(7) |
| α [°] | 90 | 67.89(3) | 90 | 76.183(1) |
| β [°] | 112.644(2) | 67.80(3) | 109.45(3) | 89.700(1) |
| γ [°] | 90 | 88.63(3) | 90 | 69.540(1) |
| *V* [ Å$^3$] | 1908.6(3) | 1057.7(5) | 2158.9(8) | 1052.6(1) |
| *Z* | 2 | 1 | 2 | 1 |
| $\rho_{calcd.}$ [g/cm$^3$] | 1.696 | 1.77 | 1.612 | 1.656 |
| μ [mm$^{-1}$] | 2.161 | 3.721 | 8.512 | 1.85 |
| *F*(000) | 1012 | 578 | 1092 | 550 |
| Index range | $-15 \leq h \leq 13$ | $0 \leq h \leq 10$ | $0 \leq h \leq 11$ | $-14 \leq h \leq 14$ |
|  | $0 \leq k \leq 24$ | $-12 \leq l \leq 12$ | $0 \leq k \leq 16$ | $-19 \leq k \leq 19$ |
|  | $0 \leq l \leq 13$ | $-12 \leq l \leq 12$ | $-13 \leq l \leq 13$ | $0 \leq l \leq 20$ |
| $\theta_{min}$, $\theta_{max}$ [°] | 1.95, 29.03 | 2.06, 23.92 | 4.55, 55.94 | 2.6, 38.54 |
| *T* [K] | 150 | 293 | 293 | 150 |
| Refl. collected | 18379 | 2860 | 2133 | 22000 |
| Refl. unique | 4738 | 2643 | 2022 | 11175 |
| R$_{int}$ | 0.021 | 0.04 | 0.078 | 0.024 |
| Refl. observed | 4304 | 2122 | 1048 | 9343 |
|  | [$F > 4.00\sigma(F)$] | [$I > 2\sigma(I)$] | [$I > 2\sigma(I)$] | [$F > 4.00\sigma(F)$] |
| *R* | 0.025 | 0.066 | 0.102 | 0.026 |
| *wR* | 0.033 | 0.077 | 0.136 | 0.032 |
| No. of variable | 351 | 244 | 191 | 406 |
| GoF | 1.168 | 1.165 | 1.205 | 0.998 |
| Larg. res. Peak [e/Å$^3$] | 0.579; −0.510 | 1.192; −1.396 | 1.031; −0.917 | 0.977; −0.798 |

their calculated positions where possible. OH hydrogen atoms were not located.

CCDC-164273 (**4**), -164274 (**3**), -164275 (**2**), and -164276 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] V. G. Makhankova, O. Yu. Vassilyeva, V. N. Kokozay, B. W. Skelton, J. Reedijk, G. A. van Albada, L. Sorace, D. Gatteschi, *New J. Chem.* **2001**, *25*, 685. [1b] V. G. Makhankova, O. Yu. Vassilyeva, V. N. Kokozay, B. W. Skelton, G. A. van Albada, J. Reedijk, *Z. Naturforsch., Teil B* **2001**, *56*, 931.

[2] [2a] E. A. Vinogradova, O. Yu. Vassilyeva, V. N. Kokozay, P. J. Squattrito, J. Reedijk, G. A. van Albada, W. Linert, S. K. Tiwary, P. R. Raithby, *New J. Chem.* **2001**, *25*, 949. [2b] E. A. Vinogradova, O. Yu. Vassilyeva, V. N. Kokozay, *Inorg. Chem. Commun.* **2002**, *5/1*, 19.

[3] E. Fenton, H. Okawa, *Chem. Ber. Recueil* **1997**, *130*, 433.

[4] [4a] V. A. Pavlenko, V. V. Skopenko, V. N. Kokozay, *Dopov. Akad. Nauk Ukr. RSR, Ser. B.* **1983**, 47. [4b] V. A. Pavlenko, V. N. Kokozay, V. V. Skopenko, *Dopov. Akad. Nauk Ukr. RSR, Ser. B* **1985**, 42. [4c] O. Yu. Vassilyeva, N. D. Nevesenko, V. V. Skopenko, Yu. S. Gerasimenko, V. N. Kokozay, *Dopov. Akad. Nauk Ukr. RSR, Ser. B* **1988**, 36. [4d] O. Yu. Vassilyeva, V. N. Kokozay, *Ukr. Khim. Zh. (Russ. Ed.)* **1993**, *59*, 176.

[5] [5a] L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, J. Reedijk, B. W. Skelton, A. G. Oliver, *J. Chem. Soc., Dalton Trans.* **1998**, 2735. [5b] L. A. Kovbasyuk, O. Yu. Vassilyeva, V. N. Kokozay, W. Linert, B. W. Skelton, A. G. Oliver, *New J. Chem.* **1998**, 931, and refs. therein.

[6] [6a] K. Smolander, *Annales Academiae Scientirum Finnicae*, Series A **1983**, *2*, 1. [6b] J. A. Bertrand, P. G. Eller, *Progr. Inorg. Chem.* **1976**, *21*, 29. S. Wang, Z. Pang, K. D. L. Smith, M. J. Wagner, *J. Chem. Soc., Dalton Trans.* **1994**, 955. [6c] A. Lehtonen, R. Sillanpaa, *J. Chem. Soc., Dalton Trans.* **1995**, 2701.

[7] J. A. Bertrand, E. Fujita, D. G. VanDerveer, *Inorg. Chem.* **1979**, *18*, 230.

[8] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, **1986**.

[9] [9a] G. A. van Albada, R. A. G. de Graaff, J. G. Haasnoot, J. Reedijk, *Inorg. Chem.* **1984**, *23*, 1404. [9b] J. G. Haasnoot, W. L. Driessen, J. Reedijk, *Inorg. Chem.* **1984**, *23*, 2803. [9c] E. Bouwman, P. Evans, R. A. G. de Graaff, H. Kooijman, R. Poinsot, P. Rabu, J. Reedijk, A. L. Spek, *Inorg. Chem.* **1995**, *34*, 6302. [9d] *Chemistry of Pseudohalides* (Eds.: A. Golub, H. Kohler, V. Skopenko), Elsevier, Amsterdam, **1986**.

[10] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227.

[11] B. J. Hathaway, D. E. Billing, *Coord. Chem. Rev.* **1970**, *5*, 143.

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

[13] [13a] T. D. Smith, J. R. Pilbrow, *Coord. Chem. Rev.* **1974**, *13*, 173. [13b] W. M. E. Koomen-van Oudenniel, R. A. G. de Graaff, J. G. Haasnoot, R. Prins, J. Reedijk, *Inorg. Chem.* **1989**, *28*, 1128. [13c] G. J. A. A. Koolhaas, W. L. Driessen, J. Reedijk, J. L. van der Plas, R. A. G de Graaff, D. Gatteschi, H. Kooijman, A. L. Spek, *Inorg. Chem.* **1996**, *35*, 1509. [13d] J. Jezierska, A. Ożarowski, G. Vučković, *Nukleonika* **1997**, *42*, 475. [13e] V. K. Voronkova, G. Vučković, J. Jezierska, J. Mroziński, Yu. V. Yablokov, *Inorg. Chim. Acta* **1997**, *262*, 147. [13f] J. Jezierska, T. Głowiak, A. Ożarowski, Yu. V. Yablokov, S. Rzaczyńska, *Inorg. Chim. Acta* **1998**, *275*, 28.

[14] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, **1970**.

[15] A. Ożarowski, unpublished program.

[16] J. Baranowski, T. Cukierda, B. Jeżowska-Trzebiatowska, H. Kozłowski, *Chem. Phys. Lett.* **1976**, *39*, 606.

[17] A. Ożarowski, D. Reinen, *Inorg. Chem.* **1986**, *25*, 1704.

[18] N. Sreehari, P. T. Manoharan, *Mol. Phys.* **1988**, *63*, 1077.

[19] F. E. Mabbs, D. Collison, *Electron Paramagnetic Resonance of d Transition Metal Compounds*, Elsevier, Amsterdam, **1992**.

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

[21] C. J. O'Connor, *Prog. Inorg. Chem.* **1982**, 29.

[22] S. R. Hall, G. S. D. King, J. M. Stewart, XTAL3.5. User's Manual, University of Western Australia: Lamb, Perth, **1995**.

[23] G. M. Sheldrick, SHELXS-86, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[24] G. M. Sheldrick, *SHELXL-93, Program for the Crystal Structure Refinement*, University of Göttingen, **1993**.

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