

# Self-assembly of the unique heterotrimetallic Cu/Co/M complexes possessing triangular antiferromagnetic $\{\text{Cu}_2\text{CoPb}\}_2$ and linear ferromagnetic $\{\text{Cu}_2\text{CoCd}_2\}$ cores†

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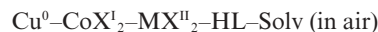
Two novel heterotrimetallic octa- $[\text{Cu}_2\text{CoPbCl}_4(\text{L})_4]_2$  (**1**) and pentanuclear  $[\text{Cu}_2\text{CoCd}_2\text{Cl}_6(\text{L})_4(\text{HOME})_2]$  (**2**) complexes have been prepared in one-pot reactions of zerovalent copper with metal chlorides in a methanol (for **1**) or acetonitrile (for **2**) solution of 2-(dimethylamino)ethanol (HL) in open air. The crystal structures of both compounds consist of discrete centrosymmetric heterotrimetallic molecules revealing triangular (**1**) and unique consecutive (**2**) arrangements of magnetic  $\text{Cu}^{\text{II}}\text{Co}^{\text{II}}$  cores. The complex **1** can be viewed as a dimer made up of tetranuclear  $\text{Cu}_2\text{CoPbCl}_4(\text{L})_4$  units linked through the two  $\mu_2$ -Cl atoms. The molecular structure of **2** is a pentanuclear assembly containing the previously unknown  $\text{Cu}(\mu\text{-O})_2\text{Co}(\mu\text{-O})_2\text{Cu}$  core. The magnetic studies of **1** revealed an antiferromagnetic coupling ( $J_{\text{CoCu}} = 37 \text{ cm}^{-1}$  and  $J_{\text{CuCu}} = 87 \text{ cm}^{-1}$ ) while **2** exhibits a weak ferromagnetic behavior ( $J_{\text{CoCu}} = -3.2 \text{ cm}^{-1}$  and  $J_{\text{CuCu}} = -14.2 \text{ cm}^{-1}$ ). The correlations between magnetic behaviour and structures as well as synthetic features are also discussed.

## Introduction

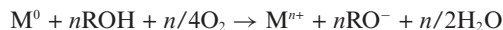
The chemistry of high-nuclearity transition metal complexes has become a very active research area in recent years.<sup>1</sup> Although a lot of work in this field has been done, a limited number of synthetic strategies have been developed to date. The use of Schiff base ligands<sup>2</sup> or rigid building blocks<sup>3</sup> provides total control over the nuclearity and geometry of the new complexes. On the other hand, spontaneous self-assembly appears to be an extremely powerful tool for the construction of novel polynuclear assemblies incorporating metal centers by utilizing the various coordination modes of small and flexible ligands.<sup>4</sup> However, this method is exceptionally sensitive to the anions<sup>5</sup> or additional ligands used.<sup>6</sup> Even crystallization conditions can have a profound effect on the structural parameters of a resulting molecule.<sup>7</sup>

Considerable research effort has been directed, over recent years, to the design and preparation of coordination metal complexes containing three different metals. This has been stimulated by a number of factors. First of all, the combination of three different spin carriers represents an excellent model for the studies of exchange interactions.<sup>8</sup> Also, there is an impressive variety of spin-coupled systems in biology, among them the heterotrimetallic Fe/Cu/Ni site in carbon monoxide dehydrogenase.<sup>9</sup>

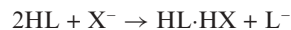
We recently described a series of heterotrimetallic Cu/Co/Ni, Cu/Co/Cd<sup>10a</sup> and Cu/Co/Zn<sup>10b,10c</sup> complexes, which were prepared in one-pot reactions of copper powder with metal salts in the presence of aminoalcohol (M = Ni, Zn, Cd; X = Cl, Br, NCS, OAc; HL = aminoalcohol):



This synthetic strategy, the direct synthesis, is based on self-assembly of building blocks, generated *in situ*, into crystalline materials. Furthermore, the employment of one of the metals in a zerovalent state enforces a bridging coordination mode of the hydroxyl groups of aminoalcohol ligand owing to their deprotonation:



This increases the likelihood of multinuclear species formation in comparison with the use of metal salts only. Of course, at least one more deprotonation mechanism of aminoalcohols can be proposed (X = various anions):



However, this model seems to play a secondary role since the stability constant for a water molecule is certainly greater than the corresponding constant for the protonated aminoalcohol  $\text{HL}\cdot\text{H}^+$ . Also, it requires an excess of aminoalcohol, as can be seen from the reaction scheme.

Based on the considerations described above and taking into account various structural and magnetic properties of a large number of heterobimetallic  $\text{Cu}^{\text{II}}/\text{Co}^{\text{II}}$  compounds,<sup>11</sup> we attempted to obtain complexes with new geometrical relationships of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  metal ions by involvement of a diamagnetic third metal ion in the resulting metal core. We have been interested in how the presence of diamagnetic metals, which possess a wide range of geometries and coordination numbers (such as  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ),

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could affect the final crystal structure and magnetic properties of heterotrimetallic Cu/Co/M assemblies.

We present here the synthesis and magnetostructural study of two novel complexes  $[\text{Cu}_2\text{CoPbCl}_4(\text{L})_4]_2$  (**1**) and  $[\text{Cu}_2\text{CoCd}_2\text{Cl}_6(\text{L})_4(\text{HOME})_2]$  (**2**) where HL is 2-(dimethylamino)ethanol. To the best of our knowledge, compound **2** represents the first example of a linear arrangement of metal centers in a  $\text{Cu}\cdots\text{Co}\cdots\text{Cu}$  core, bonded through the oxygen  $\mu_2$ -O atoms.

## Experimental

### Materials and methods

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy by the Department of Chemistry, National Taras Shevchenko University of Kyiv and with a Carlo Erba Strumentazione Analyzer (for C, H and N) by the L.V. Pisarzhevskii Institute of the Physical Chemistry.

**Synthesis of  $[\text{Cu}_2\text{CoPbCl}_4(\text{L})_4]_2$  (**1**).** Copper powder (0.32 g, 5 mmol),  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (0.6 g, 2.5 mmol),  $\text{PbCl}_2$  (1.39 g, 5 mmol), MeCN (15 mL) and 2-(dimethylamino)ethanol (2.3 mL, 23 mmol) were heated to 50–60° and stirred magnetically until the total dissolution of copper was observed (1 h). The resulting solution was filtered. Dark crystals suitable for X-ray analysis grew after 1 week. They were filtered off, washed with dry MeCN and finally dried *in vacuo* at room temperature. Yield: 0.8 g, 36% (per copper).  $\text{C}_{32}\text{H}_{80}\text{Cl}_8\text{Co}_2\text{Cu}_4\text{N}_8\text{O}_8\text{Pb}_2$  ( $M = 1775.11$ ): calcd Cu, 14.32; Co, 6.64; Pb, 23.34; C, 21.65; H, 4.54; N, 6.31. Found: Cu, 14.1; Co, 6.9; Pb, 23.6; C, 21.7; H, 4.6; N, 6.4%.

**Synthesis of  $[\text{Cu}_2\text{CoCd}_2\text{Cl}_6(\text{L})_4(\text{HOME})_2]$  (**2**).** Copper powder (0.16 g, 2.5 mmol),  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (0.6 g, 2.5 mmol),  $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$  (0.57 g, 2.5 mmol), MeOH (20 mL) and 2-(dimethylamino)ethanol (2 mL, 20 mmol) were heated to 50–60° and stirred magnetically until total dissolution of copper was observed (1 h). Dark green crystals suitable for X-ray analysis were obtained after successive addition of  $\text{Pr}^i\text{OH}$ . They were filtered off, washed with dry MeOH and finally dried *in vacuo* at room temperature. Yield: 0.35 g, 27% (per copper).  $\text{C}_{18}\text{H}_{48}\text{Cd}_2\text{Cl}_6\text{Co}_1\text{Cu}_2\text{N}_4\text{O}_6$  ( $M = 1040.25$ ): calcd Cu, 12.22; Co, 5.67; Cd, 21.61; C, 20.79; H, 4.65; N, 5.39. Found: Cu, 12.4; Co, 5.4; Cd, 21.3; C, 20.8; H, 4.7; N, 5.4%.

### EPR spectra and magnetic measurements

High frequency EPR spectra were recorded on a home-built spectrometer at the EMR facility of NHMFL.<sup>12</sup> The instrument was a transmission-type device in which waves are propagated in cylindrical lightpipes. The microwaves were generated by a Gunn oscillator, operating at  $95 \pm 3$  GHz. Frequencies higher by a factor 2, 3, or 4 were obtained using a Schottky diode-based multiplier and appropriate high-pass filters. A phase-locked oscillator (Virginia Diodes) generating a frequency of  $52 \pm 4$  GHz and its 2nd, 4th and 6th harmonics was also used. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at the magnetic induction

of 0.5 T. Corrections for the sample holders were applied. Diamagnetic corrections for the molecules ( $825 \times 10^{-6}$  for **1** and  $528 \times 10^{-6}$  cgs emu for **2**) were determined from Pascal's constants.

### IR measurements

Infrared spectra were recorded as KBr discs and in Nujol mulls on a UR-10 spectrophotometer in the 4000–400  $\text{cm}^{-1}$  region using conventional techniques.

### Crystal structure determination

Details of the data collection and processing, structure analysis and refinement are summarized in Table 1. Diffraction experiments were performed on a Bruker SMART CCD area-detector diffractometer ( $\omega$  rotation scans with narrow frames) equipped with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were corrected for Lorentz polarization effects and for the effects of absorption (multi-scan method using SADABS<sup>13</sup>). The structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  using the XTAL 3.7 program.<sup>14</sup>

In general the non-hydrogen atoms were refined anisotropically. The metal assignments were based on analytical data and coordination geometry for **1** and **2** and also from the refinement of **2**.

However, the possibility of some mixing in the metal sites can not be ruled out. All bond distances and angles within the aminoalcohol, chloride and methanol ligands are as expected.

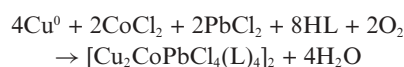
CCDC reference numbers 619313 and 619314. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612788f

## Results and discussion

### Synthesis

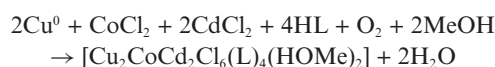
The first reactions with Cu :  $\text{CoCl}_2$  :  $\text{PbCl}_2$  in a 1 : 1 : 1 ratio resulted in dark blocks of **1** contaminated with transparent crystals which were recognized as being  $[\text{Pb}_5\text{Cl}_6(\text{L})_4]$ . This homometallic complex has been described previously.<sup>15</sup> Following a search for a more suitable initial system, the ratio 2 : 1 : 2 was used with the ligand to metal mole ratio equal to 1.8. The study of this synthetic method was repeated several times in order to confirm that the same product was consistently obtained. It may seem surprising that the optimization of the synthetic procedure of **1** required the excess of lead chloride. Presumably, some lead species forming in solution have significant influence on crystal growth and, consequently, on the purity of primary product. In contrast, the synthesis of **2** was found to be more predictable with the ratio of metals in the reaction mixture not appearing to affect the reaction product. Also, we have not detected any by-products.

The reactions were initiated and brought to completion by heating and stirring. Dark blue (**1**) or green (**2**) solutions were obtained at the end of the reactions that afforded crystals of the heterotrimetallic complexes directly (**1**) or upon successive addition of  $\text{Pr}^i\text{OH}$  (**2**). The general reaction schemes of both complexes formation can be described as follows:



**Table 1** Crystal data and structure refinement for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>32</sub> H <sub>80</sub> Cl <sub>8</sub> Co <sub>2</sub> Cu <sub>4</sub> N <sub>8</sub> O <sub>8</sub> Pb <sub>2</sub>	C <sub>18</sub> H <sub>48</sub> Cd <sub>2</sub> Cl <sub>6</sub> Co <sub>1</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>6</sub>
Formula weight	1775.11	1040.25
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	19.7380(10)	8.125(3)
<i>b</i> /Å	10.9365(9)	20.612(8)
<i>c</i> /Å	13.908(2)	11.551(4)
<i>a</i> /°	90	90
<i>β</i> /°	97.549(2)	109.099(7)
<i>γ</i> /°	90	90
<i>V</i> /Å <sup>3</sup>	2976.2(5)	1828.0(12)
<i>Z</i>	2	2
<i>D</i> (calc)/g cm <sup>-3</sup>	1.981	1.89
<i>μ</i> /mm <sup>-1</sup>	7.983	3.207
<i>F</i> (000)	1724	1030
<i>θ</i> <sub>min</sub> , <i>θ</i> <sub>max</sub> /°	1.04, 29.18	1.98, 25.0
<i>T</i> /K	150(2)	150(2)
Refl. collected	58410	16632
Refl. unique	8023	3186
<i>R</i> <sub>int</sub>	0.057	0.084
Refl. [ <i>I</i> > 2σ( <i>I</i> )]	6954	2259
<i>R</i> [ <i>I</i> > 2σ( <i>I</i> )]	0.040	0.073
w <i>R</i> (on <i>F</i> <sup>2</sup> on all data)	0.111	0.19
No. of variables	289	178
GoF	1.05	1.204



Structural features of these compounds were determined from the single-crystal X-ray data. The IR spectra of **1** and **2** in the range 4000–400 cm<sup>-1</sup> are quite similar and show all the characteristic ligand frequencies, as well as a broad ν(OH) band at 3460 cm<sup>-1</sup> associated with coordinated methanol molecules in **2**.

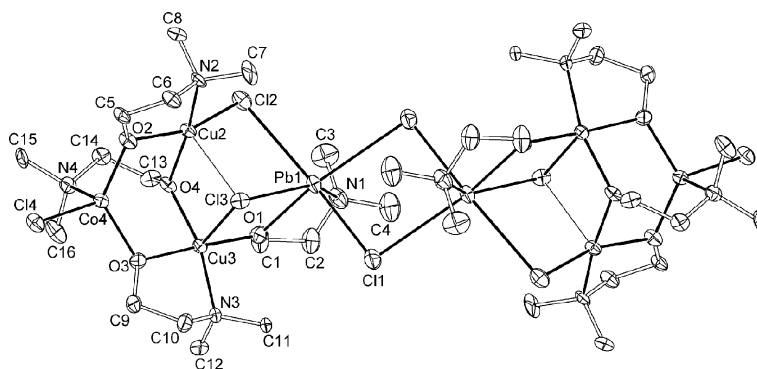
The presence of three different coordination geometries (see below) as well as the results of metal analyses corroborates the absence of metal scrambling in both complexes, while the CHN elemental analysis completely confirms their analytical purity and consistency with the proposed formulations.

### Crystal structure of **1**

The X-ray structure determination of **1** reveals a centrosymmetric octanuclear dimer (Fig. 1, Table 2) with an inversion centre located at the mid-point of the central Pb<sub>2</sub>Cl<sub>2</sub> fragment. The molecule

consists of two equivalent asymmetric Cu<sub>2</sub>CoPbCl<sub>4</sub>(L)<sub>4</sub> units linked together by two centrosymmetrically related chlorine atoms. Two copper and one cobalt atoms form an almost equilateral triangle with intermetallic angles ranging from 57.92(3)–63.38(3)° (see Fig 3). The PbCu<sub>2</sub>Co metal core is close to planar. The least-squares plane through Pb(1), Cu(2), Cu(3) and Co(4) shows that Co has the highest deviation [0.093(3)Å] and this also forms a dihedral angle of 27.16(4)° with the central Pb<sub>2</sub>Cl<sub>2</sub> plane. All metal atoms are bound by oxygen atoms from the deprotonated aminoalcohol ligands and chlorine atoms.

The two crystallographically independent copper atoms have distorted square pyramidal polyhedra fused *via* the common O(4)···Cl(3) edge. The Cu(2) possesses a NO<sub>2</sub>Cl donor set in the equatorial plane [Cu–O(N, Cl) distances are in the range 1.916(5)–2.265(2) Å; the axial Cu(2)–Cl(3) distance is 2.806(2) Å]. In contrast, Cu(3) possesses a NO<sub>3</sub> basal donor set [Cu–O(N) bond lengths vary from 1.930(5)–2.038(5) Å; the axial Cu(3)–Cl(3) length is 2.6483(16) Å]. Disregarding the very long

**Fig. 1** Molecular structure of **1** with the numbering scheme (hydrogen atoms are omitted for clarity, the non-hydrogen atoms are shown as 50% thermal ellipsoids).

**Table 2** Metal–metal distances and angles, selected bond lengths (Å) and angles (°) for **1**<sup>a</sup>

Pb(1)···Cu(2)	3.8701(8)	Cu(2)···Co(4)	3.124(1)
Pb(1)···Cu(3)	3.6133(8)	Cu(3)···Co(4)	3.151(1)
Cu(2)···Cu(3)	3.296(1)		
Pb(1)–Cl(1)	2.7230(18)	Cu(2)–N(2)	2.036(6)
Pb(1)–Cl(2)	3.1749(17)	Cu(3)–Cl(3)	2.6483(16)
Pb(1)–Cl(3)	2.9697(16)	Cu(3)–O(1)	1.931(5)
Pb(1)–O(1)	2.303(4)	Cu(3)–O(3)	1.930(5)
Pb(1)–N(1)	2.583(7)	Cu(3)–O(4)	1.978(4)
Pb(1)–Cl(1 <sup>1</sup> )	3.199(2)	Cu(3)–N(3)	2.038(5)
Cu(2)–Cl(2)	2.265(2)	Co(4)–Cl(4)	2.305(2)
Cu(2)–Cl(3)	2.8059(16)	Co(4)–O(2)	1.957(5)
Cu(2)–O(2)	1.915(5)	Co(4)–O(3)	1.965(5)
Cu(2)–O(4)	1.964(4)	Co(4)–N(4)	2.099(5)
Cu(2)···Co(4)···Cu(3)	63.38(3)	Cu(2)···Cu(3)···Co(4)	57.92(3)
Co(4)···Cu(2)···Cu(3)	58.70(3)		
Cl(1)–Pb(1)–Cl(2)	177.15(5)	Cl(3)–Cu(2)–N(2)	92.98(15)
Cl(1)–Pb(1)–Cl(3)	97.59(5)	O(2)–Cu(2)–O(4)	84.6(2)
Cl(1)–Pb(1)–O(1)	91.43(12)	O(2)–Cu(2)–N(2)	84.0(2)
Cl(1)–Pb(1)–N(1)	86.85(15)	O(4)–Cu(2)–N(2)	167.7(2)
Cl(1)–Pb(1)–Cl(1 <sup>1</sup> )	86.30(5)	Cl(3)–Cu(3)–O(1)	88.03(14)
Cl(2)–Pb(1)–Cl(3)	81.47(4)	Cl(3)–Cu(3)–O(3)	100.12(15)
Cl(2)–Pb(1)–O(1)	85.73(12)	Cl(3)–Cu(3)–O(4)	88.00(12)
Cl(2)–Pb(1)–N(1)	92.44(15)	Cl(3)–Cu(3)–N(3)	99.11(15)
Cl(2)–Pb(1)–Cl(1 <sup>1</sup> )	96.35(5)	O(1)–Cu(3)–O(3)	171.8(2)
Cl(3)–Pb(1)–O(1)	74.17(12)	O(1)–Cu(3)–O(4)	96.95(19)
Cl(3)–Pb(1)–N(1)	145.90(15)	O(1)–Cu(3)–N(3)	95.9(2)
Cl(3)–Pb(1)–Cl(1 <sup>1</sup> )	130.87(5)	O(3)–Cu(3)–O(4)	82.92(19)
O(1)–Pb(1)–N(1)	71.93(19)	O(3)–Cu(3)–N(3)	83.4(2)
O(1)–Pb(1)–Cl(1 <sup>1</sup> )	154.95(13)	O(4)–Cu(3)–N(3)	165.50(18)
N(1)–Pb(1)–Cl(1 <sup>1</sup> )	83.03(15)	Cl(4)–Co(4)–O(2)	109.98(16)
Cl(2)–Cu(2)–Cl(3)	104.11(6)	Cl(4)–Co(4)–O(3)	102.60(15)
Cl(2)–Cu(2)–O(2)	159.07(14)	Cl(4)–Co(4)–N(4)	101.14(16)
Cl(2)–Cu(2)–O(4)	95.60(14)	O(2)–Co(4)–O(3)	123.3(2)
Cl(2)–Cu(2)–N(2)	96.66(17)	O(2)–Co(4)–N(4)	106.9(2)
Cl(3)–Cu(2)–O(2)	96.73(14)	O(3)–Co(4)–N(4)	110.8(2)
Cl(3)–Cu(2)–O(4)	83.90(12)	O(4)–Co(4)–N(4)	79.04(19)

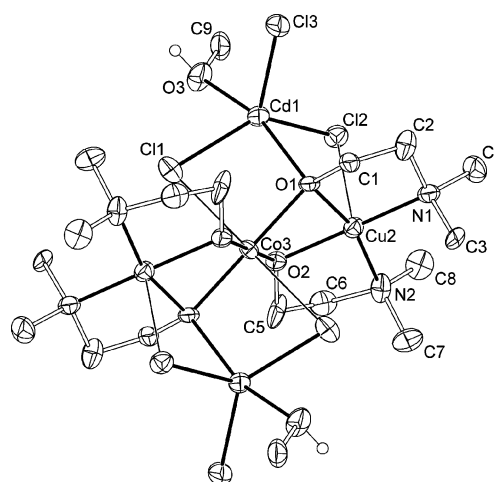
<sup>a</sup> Symmetry transformation used to generate equivalent atoms: <sup>1</sup> 1 – x, 1 – y, 1 – z.

Co(4)–O(4) bond [2.344(5) Å], the Co(4) environment could be considered distorted tetrahedral [Co–O(N) bond lengths ranging from 1.957(5)–2.099(6) Å], with the cobalt atom displaced by 0.51 Å from the O(2)–O(3)–N(4) plane towards Cl(4) resulting in a Co(4)–Cl(4) distance of 2.305(2) Å. The hexacoordinate Pb(1) presents a very distorted octahedral coordination geometry. The Pb–O(N) bond lengths are in the range from 2.303(4)–2.583(7) Å, while the Pb–Cl lengths vary from 2.723(2)–3.199(2) Å with the ‘trans’ angles ranging from 145.9(2)–177.15(5)°. Alternatively, if the lone pair is assumed to be located on the bisector of the Cl(3)–Pb(1)–Cl(1<sup>1</sup>) angle, then the coordination could be described as an almost regular pentagonal bipyramid with Cl(1) and Cl(2) occupying the axial positions and the remaining coordination atoms (Cl(1<sup>1</sup>), Cl(3), N(1), O(1)) together with a lone pair in the central plane (Fig. S1†).

The octanuclear molecules show no significant intermolecular contacts in the solid state.

### Crystal structure of **2**

The pentanuclear complex is a centrosymmetric molecule with the inversion centre situated at the Co(3) atom (Fig. 2). Relevant



**Fig. 2** Molecular structure of **2** with the numbering scheme (hydrogen atoms from the CH<sub>2</sub> and CH<sub>3</sub> groups are omitted for clarity, the non-hydrogen atoms are shown as 50% thermal ellipsoids).

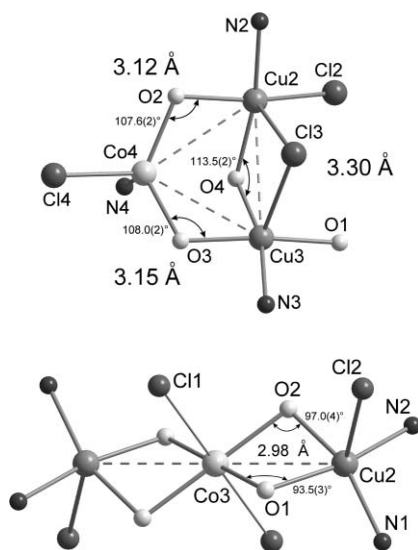
bond distances and angles are listed in Table 3. In contrast to **1**, the Cu(2), Co(3) and Cu(2') {1 – x, 1 – y, 1 – z} atoms in the

**Table 3** Metal–metal distances, selected bond lengths (Å) and angles (°) for **2**<sup>a</sup>

Cd(1)⋯Cu(2)	3.389(2)	Co(3)⋯Cu(2)	2.982(2)
Cd(1)⋯Co(3)	3.521(2)		
Cd(1)–Cl(1)	2.524(4)	Cu(2)–O(2)	1.971(9)
Cd(1)–Cl(2)	2.546(3)	Cu(2)–N(1)	2.107(11)
Cd(1)–Cl(3)	2.506(3)	Cu(2)–N(2)	2.106(11)
Cd(1)–O(1)	2.423(9)	Co(3)–Cl(1)	2.730(4)
Cd(1)–O(3)	2.369(13)	Co(3)–O(1)	2.084(8)
Cu(2)–Cl(2)	2.771(4)	Co(3)–O(2)	2.009(8)
Cu(2)–O(1)	2.009(8)		
Cl(1)–Cd(1)–Cl(2)	134.86(10)	Cl(2)–Cu(2)–N(2)	96.9(4)
Cl(1)–Cd(1)–Cl(3)	112.79(11)	O(1)–Cu(2)–O(2)	79.5(3)
Cl(1)–Cd(1)–O(1)	83.4(2)	O(1)–Cu(2)–N(1)	86.4(4)
Cl(1)–Cd(1)–O(3)	87.7(3)	O(1)–Cu(2)–N(2)	164.6(4)
Cl(2)–Cd(1)–Cl(3)	112.17(11)	O(2)–Cu(2)–N(1)	161.5(4)
Cl(2)–Cd(1)–O(1)	86.3(2)	O(2)–Cu(2)–N(2)	85.8(4)
Cl(2)–Cd(1)–O(3)	89.2(3)	N(1)–Cu(2)–N(2)	106.9(4)
Cl(3)–Cd(1)–O(1)	98.6(2)	Cl(1)–Co(3)–O(1)	85.1(3)
Cl(3)–Cd(1)–O(3)	98.9(2)	Cl(1)–Co(3)–O(2)	90.4(3)
O(1)–Cd(1)–O(3)	162.4(3)	Cl(1)–Co(3)–O(1 <sup>1</sup> )	94.9(3)
Cl(2)–Cu(2)–O(1)	89.3(3)	Cl(1)–Co(3)–O(2 <sup>1</sup> )	89.6(3)
Cl(2)–Cu(2)–O(2)	95.7(3)	O(1)–Co(3)–O(2)	76.9(3)
Cl(2)–Cu(2)–N(1)	96.2(3)	O(1)–Co(3)–O(2 <sup>1</sup> )	103.1(3)

<sup>a</sup> Symmetry transformation used to generate equivalent atoms: <sup>1</sup> 1 – *x*, 1 – *y*, 1 – *z*.

Cu<sub>2</sub>CoCdO<sub>4</sub>Cl<sub>2</sub> core are now located on a straight line with the Co(3)⋯Cu(2) distance equal to 2.982(2) Å (Fig. 3).



**Fig. 3** Perspective views of the Cu–Co cores of complexes **1** (top) and **2** (bottom) showing the metal centers and donor atoms as well as the intermetal distances and M–O–M angles.

The Co(3) atom adopts an approximate square-planar environment but with relatively long Co(3)–Cl(1) bonds of 2.730(4) Å, thus forming an elongated octahedron. The Cu(2) metal atom in the N<sub>2</sub>O<sub>2</sub> site has a distorted square pyramidal geometry with a chlorine atom in the apical site [Cu–O(N) distances are in the range of 1.971(9)–2.107(11) Å]. The Cd atom possesses a distorted trigonal bipyramidal environment [the O(3)–Cd(1)–O(1) angle is 162.4(3)°] with the equatorial plane consisting of chlorine atoms and axial positions occupied by the oxygen from the aminoalcohol

ligand and by the methanol molecule. The OH group of the coordinated methanol molecule forms a weak intermolecular hydrogen bond to Cl(3) of a centrosymmetrically-related molecule [O(3)⋯Cl(3<sup>1</sup>) {1 – *x*, 1 – *y*, –*z*} 3.19(1) Å, H(3)⋯Cl(3<sup>1</sup>) 2.55 Å, O(3)–H⋯Cl(3<sup>1</sup>) 127.0°] to build a one-dimensional chain along the *c* axis (Fig. S2†).

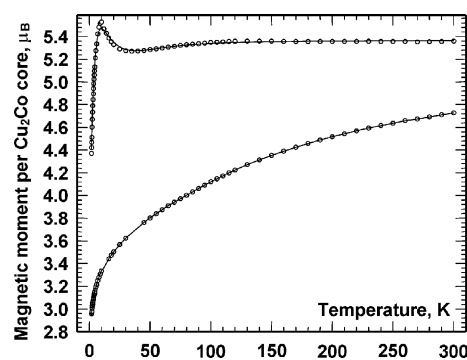
### EPR spectra

Complex **1** exhibits spectra of very low intensity and quality leading us to conclude that it is likely that we are only observing spectra of monomeric impurities containing high-spin Co<sup>2+</sup>. Compound **2** seems to be EPR silent as well. The only reproducible feature was a weak but characteristic spectrum of uncoupled Cu<sup>2+</sup> ion with *g*<sub>*x,y*</sub> = 2.051 and *g*<sub>*z*</sub> = 2.237 which was visible at each frequency between 95 and 336 GHz and at all temperatures (4–300 K). This spectrum is most likely due to a monomeric impurity.

### Magnetic properties

Both compounds contain trinuclear units in which two copper atoms may interact with one cobalt atom and with each other. It is assumed that the two Cu<sub>2</sub>Co cores in **1** do not interact with each other as they are separated by long bridges containing five atoms (Cl–Pb–Cl–Pb–Cl). For easy comparison of **1** and **2**, the magnetic moments presented in Fig. 4 refer to half of the molar mass of **1** but to the whole molar mass of **2**. Description of magnetic interactions is difficult, in particular in the absence of supporting EPR data, and some simplifying assumptions must be made. We assume that in both complexes the two copper atoms interacting with cobalt are equivalent—this is true for **2**, but not necessarily true for **1**. The Hamiltonian for the exchange interactions thus may be written as

$$H = J_{\text{CoCu}}(S_{\text{Co}}S_{\text{Cu1}} + S_{\text{Co}}S_{\text{Cu2}}) + J_{\text{CuCu}}S_{\text{Cu1}}S_{\text{Cu2}}$$



**Fig. 4** Magnetic moment of **1** (bottom) and of **2** (top). Circles are the experimental points, while solid lines were calculated with *g*<sub>Co</sub> = 2.23(1), *D*<sub>Co</sub> = –6.5(3) cm<sup>–1</sup>, *J*<sub>CoCu</sub> = 38(1) cm<sup>–1</sup>, *J*<sub>CuCu</sub> = 89(2) cm<sup>–1</sup> for **1** and *g*<sub>Co</sub> = 2.40(1), *D*<sub>Co</sub> = 56(2) cm<sup>–1</sup>, *J*<sub>CoCu</sub> = –3.2(3) cm<sup>–1</sup>, *J*<sub>CuCu</sub> = –14(3) cm<sup>–1</sup>, *D*<sub>CoCu</sub> = 8.8(2) cm<sup>–1</sup> for **2** (see text).

In this notation, antiferromagnetic interaction has positive *J*. Application of the simple Kambe's method<sup>16</sup> gives energies of the four possible states of the total spin *S*: *E*<sub>5/2</sub> = (3/2)*J*<sub>CoCu</sub> + (1/4)*J*<sub>CuCu</sub>, *E*<sub>3/2</sub><sup>a</sup> = –*J*<sub>CoCu</sub> + (1/4)*J*<sub>CuCu</sub>, *E*<sub>3/2</sub><sup>b</sup> = –(3/4)*J*<sub>CuCu</sub> and *E*<sub>1/2</sub> = –(5/2)*J*<sub>CoCu</sub> + (1/4)*J*<sub>CuCu</sub>. The magnetic susceptibility of a

CoCuCu entity can then be fitted to the formula

$$\chi = \frac{N\mu_B^2 g^2}{3kT} \frac{\sum_{i=1}^4 (2S_i + 1)(S_i + 1)S_i \exp(-E_i/kT)}{\sum_{i=1}^4 (2S_i + 1) \exp(-E_i/kT)} + \text{TIP}$$

Fitting the data of **1** gives  $J_{\text{CoCu}} = 22 \text{ cm}^{-1}$ ,  $J_{\text{CuCu}} = 54 \text{ cm}^{-1}$ ,  $g = 2.0$ ,  $\text{TIP} = 1130 \times 10^{-6}$ . The energies of the four states above are 46.5,  $-8.5$ ,  $-40.5$ ,  $-41.5 \text{ cm}^{-1}$ , respectively. The values of  $g$  and TIP are not reasonable and moreover, the method fails completely for compound **2**. The likely explanation is that high-spin cobalt ( $S = 3/2$ ) may have very large zero-field splitting, comparable to the exchange integrals, that will affect susceptibility, particularly at the lower temperatures. Also, the exchange interactions Co–Cu may be anisotropic and contribute to the zero-field splitting. To account for these effects one can expand the spin Hamiltonian:

$$\begin{aligned} H = & J_{\text{CoCu}}(\mathbf{S}_{\text{Co}}\mathbf{S}_{\text{Cu1}} + \mathbf{S}_{\text{Co}}\mathbf{S}_{\text{Cu2}}) + J_{\text{CuCu}}\mathbf{S}_{\text{Cu1}}\mathbf{S}_{\text{Cu2}} \\ & + D_{\text{Co}}\{\mathbf{S}_{\text{zCo}}^2 - 1/3\mathbf{S}_{\text{Co}}(\mathbf{S}_{\text{Co}} + 1)\} + D_{\text{CoCu}}(\mathbf{S}_{\text{zCo}}\mathbf{S}_{\text{zCu1}} \\ & + \mathbf{S}_{\text{zCo}}\mathbf{S}_{\text{zCu2}} - 1/3\mathbf{S}_{\text{Co}}\mathbf{S}_{\text{Cu1}} - 1/3\mathbf{S}_{\text{Co}}\mathbf{S}_{\text{Cu2}}) \\ & + \mu_B B(g_{\text{Co}}\mathbf{S}_{\text{Co}} + g_{\text{Cu1}}\mathbf{S}_{\text{Cu1}} + g_{\text{Cu2}}\mathbf{S}_{\text{Cu2}}) \end{aligned}$$

The anisotropy of the Cu–Cu exchange interactions is not expected to contribute more than  $\sim 1 \text{ cm}^{-1}$  to the zero-field splitting and was neglected.<sup>17</sup> The energies of the 16 levels in the system are calculated by numerical diagonalization of the entire  $16 \times 16$  spin Hamiltonian matrix. The magnetic susceptibility related to one CuCoCu unit is then calculated from the formula

$$\chi = -\frac{N}{B} \frac{\sum_{i=1}^{16} \frac{\partial E_i}{\partial B} \exp(-E_i/kT)}{\sum_{i=1}^{16} \exp(-E_i/kT)} + \text{TIP}$$

in which the derivatives  $\partial E_i/\partial B$  must be calculated numerically. The  $g_{\text{average}}$  value for Cu was assumed equal to 2.113 while  $g_{\text{Co}}$  was fitted. TIP was fixed at  $270 \times 10^{-6}$  cgs emu, expected for the sum of two  $\text{Cu}^{2+}$  ions and one  $\text{Co}^{2+}$  ion. A reasonable fitting could be achieved for **1** without taking into account the term with  $D_{\text{CoCu}}$ . The following fitted parameters were obtained:  $g_{\text{Co}} = 2.23(1)$ ,  $D_{\text{Co}} = -6.5(3) \text{ cm}^{-1}$ ,  $J_{\text{CoCu}} = 38(1) \text{ cm}^{-1}$ ,  $J_{\text{CuCu}} = 89(2) \text{ cm}^{-1}$ . Magnetic properties of **2** are drastically different from **1** and it was necessary to allow a non-zero value of  $D_{\text{CoCu}}$  to reproduce the peculiar temperature dependence of its magnetic moment. The fitting procedure gave  $g_{\text{Co}} = 2.40(1)$ ,  $D_{\text{Co}} = 56(2) \text{ cm}^{-1}$ ,  $J_{\text{CoCu}} = -3.2(3) \text{ cm}^{-1}$ ,  $J_{\text{CuCu}} = -14(3) \text{ cm}^{-1}$ ,  $D_{\text{CoCu}} = 8.8(2) \text{ cm}^{-1}$ . The very large value of  $D_{\text{CoCu}}$ , compared to  $J_{\text{CoCu}}$  indicates that the exchange interactions Co–Cu are very strongly anisotropic. A theory of anisotropic exchange interactions has been formulated for Cu–Cu pairs,<sup>18</sup> but not, to our knowledge, for interactions involving high-spin ions. It is therefore difficult to assess the plausibility of the  $D_{\text{CoCu}}$  value and we can only say that we cannot reproduce the magnetic properties of **2** without it. Qualitatively, the difference in  $D_{\text{Co}}$  magnitudes in **1** and **2** can be rationalized. It is known that high-spin  $\text{Co}^{2+}$  shows in tetrahedral geometry moderately large zero-field splitting of several wavenumbers<sup>19</sup> while extremely large splittings of sometimes hundreds of wavenumbers were observed in octahedral geometry.<sup>20</sup> Also, the pattern of exchange interactions appears to be in agreement with the structures—in **1** the angles Cu(3)–O(4)–Cu(2), Cu(2)–O(2)–Co(4) and Cu(3)–O(3)–Co(4) are 113.5(2), 107.6(2) and 108.0(2)°, respectively, thus favoring antiferromagnetic exchange interactions. In **2**, it may appear surprising that  $J_{\text{CuCu}}$  is calculated to be larger than  $J_{\text{CoCu}}$ . A possible explanation is that the angles [93.5(3)° for

Cu(2)–O(1)–Co(3) and 97.0(4)° for Cu(2)–O(2)–Co(3)] are close to the borderline separating antiferromagnetic interactions from ferromagnetic interactions (which is 97° in the better-known CuOCu systems), result in a  $J_{\text{CuCo}}$  value close to zero. On the other hand, the Cu–Cu interactions through an intervening metal atom may be surprisingly strong, as observed by us recently in a simpler Cu–O–Zn–O–Cu system,<sup>4</sup> in which  $J_{\text{CuCu}}$  is 35  $\text{cm}^{-1}$ . It should be emphasised that the magnetic moments of **1** and **2** cannot be reproduced without introducing the zero-field splitting on cobalt ions, and in **2** inclusion of the anisotropy of the Cu–Co exchange interactions also appears necessary. However, fitting the relatively featureless temperature dependences of magnetic moments or susceptibilities is always risky, since multiple  $\chi^2$  minima of similar quality may exist. It is known, for example in cases much simpler than the present one, that magnetic fitting is not sensitive to the sign of  $D$  in monomeric high-spin cobalt and nickel complexes.<sup>21</sup> In our case, the fit for **1** can indeed converge to either positive  $D_{\text{Co}} = 6.3 \text{ cm}^{-1}$  or to  $D_{\text{Co}} = -6.5 \text{ cm}^{-1}$  with other parameters only slightly altered. We tried to keep the number of parameters at the minimum sufficient to reproduce the experimental data yet we could not avoid parameter correlation and ambiguity as described above.

## Conclusions

All coordination compounds belong to a limited set of molecular structure types that are determined by the nature of metal centres, except in those cases where a ligand unambiguously predefines the nuclearity of a complex.<sup>22</sup> The arrangement of eight polyhedra in **1** represents a rare molecular structure type since the complexes containing more than six metal centers commonly possess ring or cage structures.<sup>23</sup> However, considering the dimeric nature of **1**, one may view it as a derivative of the well-known tetranuclear  $\text{M}_4\text{X}_6\text{Y}_n$  core ( $\text{X}_6$  are bridging atoms and  $\text{Y}_n$  are terminal atoms, where  $n$  depends on a metal's polyhedra). The use of the synthetic procedure described for **1** with a replacement of a  $\text{PbCl}_2$  by  $\text{CdCl}_2$  affords the easy self-assembly of a new pentanuclear complex **2**. Although the molecular structure type observed in **2** is known<sup>5a,22c</sup> it has never been utilized for the preparation of heterotrimetallic complexes. Furthermore, a  $\text{Cu}(\mu\text{-O})_2\text{Co}(\mu\text{-O})_2\text{Cu}$  fragment in **2** represents, as far as we are aware, the first example of a consecutive arrangement of a  $\text{Cu}_2\text{Co}$  core.

Both compounds exhibit quite different geometrical relationships between paramagnetic metal centres in a  $\text{Cu}_2\text{Co}$  core and therefore different magnetic behaviour: triangular geometry for **1** (antiferromagnetic) and linear for **2** (ferromagnetic). The third diamagnetic metal (Pb or Cd) affects the crystal structure of complex formed and hence indirectly predetermines the magnetic properties of the resulting heterometallic assembly.

Finally, although the correlation between initial components and final molecular structure becomes difficult with an increasing number of components, it is clear that spontaneous self-assembly is an easy and effective pathway for the synthesis of spin-coupled metal assemblies.

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