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# Novel heterometallic Cd/Cu complexes prepared using zerovalent copper: control of the nuclearity and structural diversity by halide counterions

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Three kinds of $Cd^{II}/Cu^{II}$ compounds of different nuclearity: tetranuclear $[Cd_2Cu_2I_4L_4(dmso)_2]$ **1**, pentanuclear $[Cd_2Cu_3Br_6L_4(dmso)_2]$ **2** and hexanuclear $[Cd_4Cu_2Cl_6L_6(H_2O)_2]$ **3**, have been synthesised by the reaction of zerovalent copper and cadmium halides with non-aqueous (dmso, $CH_3CN$) solutions of 2-dimethylaminoethanol (HL) in air. The choice of counteranion in the initial cadmium salt provides a useful method of altering the nuclearity and structure of the heterometallic Cd/Cu complexes. Crystallographic investigations reveal that **1** has a centrosymmetric tetranuclear structure with a zig-zag Cd–Cu–Cu–Cd skeleton. The molecular structure of **2** consists of a pentanuclear centrosymmetric core in which four metal atoms are linked together by bridging oxygen atoms of L groups and bromide anions to form a parallelogram Cu–Cd–Cu–Cd centred on the fifth Cu. The hexanuclear complex **3** is made up of two symmetry-related units with triangular $CuCd_2$ cores linked by amino alkoxo bridges, involving cadmium centres of both units.

## Introduction

The field of high nuclearity complexes is a source of great interest with long term potential applications as new materials that exhibit novel physical and magnetic properties.[1] Although various preparative methods have been proposed in order to obtain polynuclear complexes a 'rational' synthetic approach to new compounds is still one of the major challenges for inorganic chemists. The use of polynucleating ligands and complexes as ligands can provide an efficient route to gain control of the nuclearity and dimensionality of the polymetallic architecture.[2] Synthetic difficulties in obtaining elaborate ligands and molecular synthons that can be used as ligands are a critical factor in restricting further studies because of the often tedious, costly, multi-step procedures that afford these ligands in low yield.

Our systematic study has demonstrated that amino alcohols represent a powerful tool for assembling polynuclear metal complexes in 'one pot' reactions using zerovalent metals as starting materials.[3] The background to such a synthetic strategy was established in the investigations of the dissolution of metal powders ($Cu^0$, $Ni^0$, $Zn^0$) in the presence of ammonium salts, in air, to form metal complexes as summarised in the following reaction scheme:[4]

$$M^0 + 2NH_4^+ + 1/2O_2 \longrightarrow M^{2+} + H_2O + 2NH_3 \quad (1)$$

The metal oxidation and complex formation were conditioned by the presence of a proton-donating agent (ammonium salt) and dioxygen from the air which was reduced to give $H_2O$. The synthetic route was further developed to yield heterometallic complexes, and involved the reaction of copper powder with a salt of another metal in non-aqueous solution of amino alcohol that was known to be a very efficient proton-donating agent. This approach yielded various Cu/M complexes, including Cu/Pb,[3a] and those containing Co,[3b] Ni [3c] as the second metal, for example:

$$2Cu^0 + 2PbX_2 + 4HL + O_2 + n\text{Solv} \longrightarrow [Cu_2Pb_2X_4(L)_4]\cdot n\text{Solv} + 2H_2O \quad (2)$$

$$2Cu^0 + 2CoX_2 + 8H_2L + 1.5O_2 + n\text{Solv} \longrightarrow [Cu^{II}_2Co^{III}_2(H_2L)_2(L)_4]X_2\cdot n\text{Solv} + 2H_2L\cdot HX + 3H_2O \quad (3)$$

$$4Cu^0 + 2CoX_2 + 6HL + 2O_2 + n\text{Solv} \longrightarrow [Cu_2Co(\mu_3\text{-}OH)X_2L_3]_2\cdot n\text{Solv} + 2H_2O \quad (4)$$

$$2Cu^0 + 3NiX_2 + 8HL + O_2 \xrightarrow{\text{Solv}} [Cu_2Ni_3X_4(L)_6] + 2HL\cdot HX + 2H_2O \quad (5)$$

where X = Cl, Br, I, SCN, $O_2CMe$; Solv = dmf, dmso, $CH_3CN$, $CH_3OH$; HL = 2-aminoethanol (Cu/Pb complexes), 2-dimethylaminoethanol; $H_2L$ = diethanolamine.

The principal aims of these studies have been the preparation of a broad range of species containing a variety of mixed-metal stoichiometries and the investigation of the dependence of the individual structures and mixed-metal stoichiometries on the reaction system employed. Recently, we have reported the synthesis of trinuclear $Cu_2Zn$ complexes with incomplete cube-like cores of Cu, Zn, X (X = Cl, Br, I, SCN) with O atoms from 2-dimethylaminoethanol (HL) formed directly from zerovalent metal powders or metallic copper and zinc oxide.[5] In a continuation of this work, we explored the reaction of copper powder, a cadmium salt and HL in solution (dmso, $CH_3CN$) in air. Herein we report the isolation and structural characterization

**Table 1** Crystal data and structure refinement for **1**–**3**

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{20}H_{52}Cd_2Cu_2I_4N_4O_6S_2$ | $C_{20}H_{52}Br_6Cd_2Cu_3N_4O_6S_2$ | $C_{24}H_{64}Cd_4Cl_6Cu_2N_6O_8$ |
| Formula weight | 1368.32 | 1403.67 | 1354.26 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $C2/c$ | $P2_1/n$ |
| $a$/Å | 8.4240(3) | 31.395(2) | 8.835(2) |
| $b$/Å | 18.1880(7) | 8.0019(6) | 11.865(2) |
| $c$/Å | 13.4520(5) | 18.7480(10) | 21.463(4) |
| $\beta$/° | 97.576(2) | 118.1070(10) | 91.105(5) |
| $V$/Å$^3$ | 2043.07(13) | 4154.4(5) | 2249.5(8) |
| $Z$ | 2 | 4 | 2 |
| $T$/K | 150 | 150 | 150 |
| $\mu$/mm$^{-1}$ | 5.212 | 8.425 | 3.187 |
| $R_{int}$ | 0.0837 | 0.065 | 0.052 |
| Measured/independent reflections | 35254/4670 | 30649/5514 | 42980/11309 |
| Data used | 3160 [$I > 2\sigma(I)$] | 4002 [$F > 4\sigma(F)$] | 8499 [$F > 4\sigma(F)$] |
| $R$ | 0.0412 | 0.035 | 0.046 |
| w$R$ | 0.0877 (all data) | 0.037 | 0.054 |

of three kinds of $Cd^{II}/Cu^{II}$ compounds with different nuclearities – tetranuclear $[Cd_2Cu_2I_4L_4(dmso)_2]$ **1**, pentanuclear $[Cd_2Cu_3Br_6L_4(dmso)_2]$ **2** and hexanuclear $[Cd_4Cu_2Cl_6L_6(H_2O)_2]$ **3** – that have a number of interesting features. Remarkably, of the few published structures that contain both metals most are polymers of various dimensionality[6] or contain halocadmate anions.[7] Higher nuclearity species are limited to two examples with $CdCu_2$[8a] and $Cd_2Cu_2$[8b] metal cores.

## Experimental

### General details

Commercial reagents were used without further purification, all experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy, by standard titrimetric methods for anions and by the Department of Chemistry, University of Bath microanalytical service (for C, H and N). Infrared spectra (4000–400 cm$^{-1}$) were recorded as KBr discs with a UR-10 spectrophotometer. X-Band solid-state EPR spectra were measured using a Radiopan PS100.X spectrometer.

### Preparations

**$[Cd_2Cu_2I_4L_4(dmso)_2]$ (1).** Copper powder (0.16 g, 2.5 mmol), $CdI_2$ (1.82 g, 5 mmol), dmso (20 cm$^3$) and 2-dimethylaminoethanol (2 cm$^3$) were heated to 50–60 °C and magnetically stirred until total dissolution of $Cu^0$ and $CdI_2$ was observed (100 min). The resulting blue solution was filtered and allowed to stand at room temperature. Dark-blue microcrystals of **1** were formed after one day. They were collected by filter-suction and dried *in vacuo*. Yield: 0.77 g, 45%. Anal. calc. for $C_{20}H_{52}Cd_2Cu_2I_4N_4O_6S_2$: C, 17.56; H, 3.83; N, 4.09; Cu, 9.29; Cd, 16.43; I, 37.10. Found: C, 17.60; H, 3.80; N, 4.01; Cu, 10.0; Cd, 16.8; I, 36.9%. IR (KBr, cm$^{-1}$): 3500br, 3000m, 2980w, 2910sh, 2890sh, 2860m, 2845s, 2815sh, 1630br, 1460m, 1430sh, 1405w, 1380w, 1355w, 1315w, 1290w, 1285w, 1250w, 1180w, 1095s, 1085s, 1020s, 955s, 900s, 790m, 720w, 640m, 515m, 470w, 440w.

**$[Cd_2Cu_3Br_6L_4(dmso)_2]$ (2).** This complex was obtained in a similar way to that of **1**, but $CdI_2$ was replaced by $CdBr_2·4H_2O$. Dark-green crystals suitable for X-ray crystallography were deposited in two weeks after the successive additions of Pr$^i$OH into the resulting blue solution. Yield: 0.7 g, 59%. Anal. calc. for $C_{20}H_{52}Br_6Cd_2Cu_3N_4O_6S_2$: C, 17.11; H, 3.73; N, 3.99; Cu, 13.58; Cd, 16.02; Br, 34.16. Found: C, 17.62; H, 3.84; N, 3.93; Cu, 13.5; Cd, 16.1; Br, 34.0%. IR (KBr, cm$^{-1}$): 3500br, 3000m, 2980m, 2900m, 2860m, 2820m, 1620br, 1465m, 1430w, 1410w, 1380sh, 1350w, 1310w, 1285w, 1250w, 1190w, 1105m, 1060s, 1025s, 950s, 910m, 790m, 750w, 715w, 655m, 620w, 520w, 485m, 440w.

**$[Cd_4Cu_2Cl_6L_6(H_2O)_2]$ (3).** This complex was obtained in a similar manner to that of **1** except for the use of $CdCl_2·2.5H_2O$ instead of $CdI_2$ in $CH_3CN$ (20 cm$^3$). Dark-blue prisms suitable for X-ray diffraction studies were obtained from the reaction mixture in the presence of Pr$^i$OH after 20 days. Yield: 0.72 g, 41%. Anal. calc. for $C_{24}H_{64}Cd_4Cl_6Cu_2N_6O_8$: C, 21.29; H, 4.76; N, 6.21; Cu, 9.38; Cd, 33.20; Cl, 15.71. Found: C, 22.17; H, 4.89; N, 6.08; Cu, 9.40; Cd, 33.25; Cl, 15.68%. IR (KBr, cm$^{-1}$): 3370s, 3010sh, 2970m, 2910m, 2895s, 2875s, 2865s, 2810m, 1720w, 1610w, 1465s, 1405w, 1380w, 1350w, 1280m, 1255w, 1185m, 1105sh, 1085vs, 1050sh, 1030s, 955s, 905m, 880m, 785m, 620m, 570m, 505m, 475m, 440m.

The compounds are insoluble in water and sparingly soluble in dmf and dmso.

### X-Ray crystallography

Diffraction experiments were performed on a Nonius Kappa CCD diffractometer (**1**) and a Siemens SMART CCD diffractometer ($\omega$ rotation scans with narrow frames) (**2**, **3**), all using graphite monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). The data were corrected for Lorentz-polarization effects and for the effects of absorption (multi-scans). The structures were solved by direct methods and refined by full-matrix, least-squares methods on $F^2$ (**1**) and $F$ (**2**, **3**) using SHELXL-97[9] and XTAL3.7,[10] respectively. The non-hydrogen atoms were refined anisotropically, hydrogen atoms included but not refined. Disorder of three C atoms of one L group in **1** was modelled in terms of two sets of positions with occupancy set to 0.35 and 0.65 after initial refinement. The S atom of dmso in **2** was disordered over two sites with occupancy refined to 0.884(5) and 0.116(5), with the constraint that the two components sum to unity. The crystallographic data, data collection and refinement parameters are collected in Table 1.

CCDC reference numbers 178072–178074.

See http://www.rsc.org/suppdata/dt/b2/b205917g/ for crystallographic data in CIF or other electronic format.

## Results and discussion

### Syntheses and spectroscopic characterization

The reaction of copper powder with cadmium halides and 2-dimethylaminoethanol in a non-aqueous solvent, in air, using a molar ratio of $Cu:CdX_2:HL$ = 1:2:6 (HL = $HMe_2Ea$; X = Cl, Br, I) gave mixed-metal compounds which show analytical data accounting for the presence of Cd(II) and Cu(II) in a 1:1, 1:1.5 and 2:1 stoichiometry for **1**, **2** and **3**, respectively. The ratio of

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

| | | | |
|---|---|---|---|
| Cd(1)–O(21) | 2.216(4) | Cu(1)–O(11) | 1.915(4) |
| Cd(1)–O(31) | 2.481(4) | Cu(1)–O(11a) | 1.952(4) |
| Cd(1)–N(24) | 2.401(5) | Cu(1)–O(21) | 1.881(4) |
| Cd(1)–I(1) | 2.7580(6) | Cu(1)–O(31) | 2.335(4) |
| Cd(1)–I(2) | 2.7395(6) | Cu(1)–N(14) | 2.055(5) |
| O(21)–Cd(1)–O(31) | 70.07(13) | O(21)–Cu(1)–O(11) | 174.36(18) |
| O(21)–Cd(1)–N(24) | 73.62(16) | O(21)–Cu(1)–O(11a) | 99.04(17) |
| N(24)–Cd(1)–O(31) | 143.66(15) | O(11)–Cu(1)–O(11a) | 79.20(18) |
| O(21)–Cd(1)–I(2) | 124.41(11) | O(21)–Cu(1)–N(14) | 99.0(2) |
| N(24)–Cd(1)–I(2) | 99.85(13) | O(11)–Cu(1)–N(14) | 84.93(19) |
| O(31)–Cd(1)–I(2) | 99.22(10) | O(11a)–Cu(1)–N(14) | 149.49(19) |
| O(21)–Cd(1)–I(1) | 121.05(11) | O(21)–Cu(1)–O(31) | 79.00(15) |
| N(24)–Cd(1)–I(1) | 105.16(13) | O(11)–Cu(1)–O(31) | 96.65(16) |
| O(31)–Cd(1)–I(1) | 94.79(11) | O(11a)–Cu(1)–O(31) | 112.37(17) |
| I(2)–Cd(1)–I(1) | 114.00(2) | N(14)–Cu(1)–O(31) | 95.14(19) |

[a] Symmetry transformation used to generate equivalent atoms: $-x + 2, -y + 2, -z + 1$.

metals in the reaction mixture does not appear to influence the reaction product. The structural features of these complexes were determined by IR spectroscopy and from single-crystal X-ray diffraction studies.

The IR spectra of complexes **1**, **2** and **3** in the range 4000–400 cm$^{-1}$ are quite similar and show all the characteristic ligand peaks. Bands corresponding to $\nu$(SO) vibrations of dmso molecules expected in the region 1100–900 cm$^{-1}$ in the spectra of **1** and **2** cannot be detected possibly due to overlapping with intense bands of L groups. The very strong broad $\nu$(OH) vibration at *ca.* 3370 cm$^{-1}$ and the weak $\delta(H_2O)$ absorption at 1610 cm$^{-1}$ of water molecules can be identified easily for **3**. The polycrystalline powder EPR spectra of **1**–**3** at room temperature are essentially similar and show a broad single line near $g = 2.07$. No sharpening of the lines or hyperfine splitting is observed upon cooling from room temperature to 77 K. These data confirm the presence of paramagnetic centres but do not provide useful information regarding the formulation or structures of the materials.

## Description of the structure of 1

Complex **1**, $[Cd_2Cu_2I_4L_4(dmso)_2]$, exhibits a centrosymmetric tetranuclear structure with a zig-zag Cd–Cu–Cu–Cd skeleton (Fig. 1). Selected bond lengths and angles are listed in Table 2. The molecule sits on a crystallographic inversion centre at the mid-point of the central $Cu_2O_2$ unit. The four metal atoms are doubly bridged by six oxygen atoms of the four L groups and two dmso molecules with the metal–metal separations being 3.476(2) and 2.980(1) Å for Cu ··· Cd and Cu ··· Cu, respectively. The central copper(II) atoms have distorted square-pyramidal coordination to a $NO_3O_{(dmso)}$ donor set. The four copper–ligand bonds in the plane vary between 1.881(4) and 2.055(5) Å, while the axial bond to bridging oxygen atom O(31) of the dmso molecule is elongated [2.335(4) Å]. The local geometry at the terminal Cd atoms is distorted trigonal bipyramidal with two iodide anions and a bridging oxygen atom from L group, O(21), in the equatorial plane and the apical positions occupied by the nitrogen of the L group, N(24), and the bridging oxygen atom, O(31), from the dmso molecule. The N(24)–Cd(1)–O(31) angle of 143.7(2)° shows that the three atoms are far from linear. The origin for this large deviation from linearity involves the participation of the dmso oxygen in bridging copper and cadmium centres, the first example, to our knowledge, of such a bridging mode between heteronuclear metal atoms.

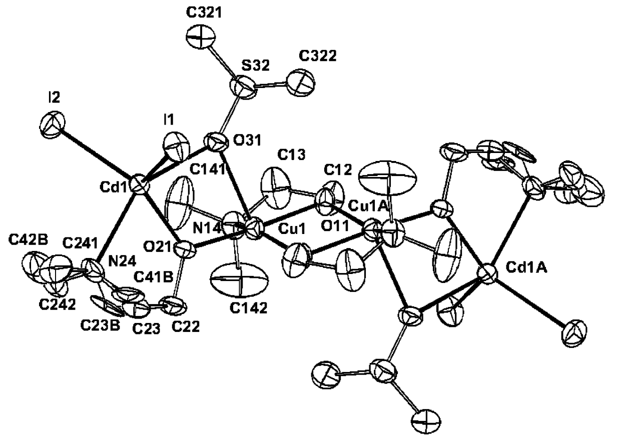

**Fig. 1** Molecular structure of complex **1**, showing the atom numbering, with 50% probability displacement ellipsoids.

## Description of the structure of 2

Complex **2** consists of pentanuclear centrosymmetric molecules $[Cd_2Cu_3Br_6L_4(dmso)_2]$, with the central copper atom, Cu(1), located on an inversion centre (Fig. 2). Selected bond lengths and angles are listed in Table 3. Cu(1) adopts a six-coordinate environment by interacting with four oxygen atoms from L groups [average 1.958(3) Å] in the equatorial plane and two axially disposed bridging bromide anions, Br(1) and Br(1a), at 3.0688(6) Å. The two other Cu atoms, related by the inversion centre have square-pyramidal environments with apical elongation. The donor atoms of the two L groups are placed in the

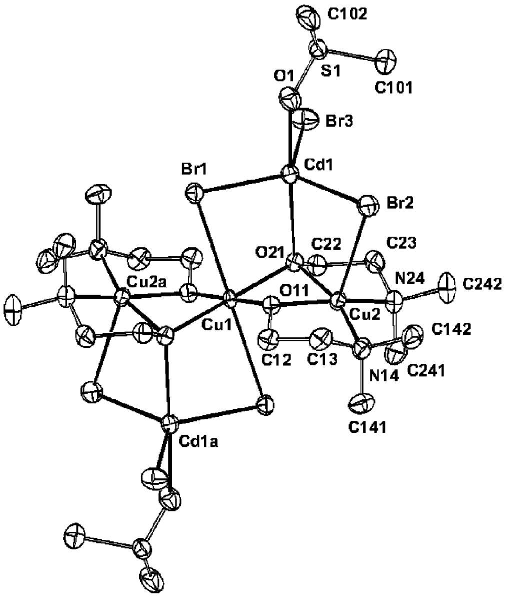

**Fig. 2** Molecular structure of complex **2**, showing the atom numbering, with 50% probability displacement ellipsoids.

**Table 3** Selected bond distances (Å) and angles (°) for **2**[a]

| | | | |
|---|---|---|---|
| Cd(1)–O(1) | 2.374(4) | Cu(1)–Br(1) | 3.0688(6) |
| Cd(1)–O(21) | 2.504(4) | Cu(2)–O(11) | 1.913(3) |
| Cd(1)–Br(1) | 2.5733(6) | Cu(2)–O(21) | 1.980(3) |
| Cd(1)–Br(2) | 2.6056(6) | Cu(2)–N(14) | 2.091(5) |
| Cd(1)–Br(3) | 2.5821(9) | Cu(2)–N(24) | 2.069(4) |
| Cu(1)–O(11) | 1.918(3) | Cu(2)–Br(2) | 2.8300(9) |
| Cu(1)–O(21) | 1.997(3) | | |
| | | | |
| O(21)–Cd(1)–O(1) | 168.8(1) | Br(1)–Cu(1)–O(11) | 87.9(1) |
| Br(1)–Cd(1)–O(1) | 92.17(8) | Br(1)–Cu(1)–O(21a) | 95.0(1) |
| Br(1)–Cd(1)–O(21) | 87.53(7) | Br(1)–Cu(1)–O(21) | 85.0(1) |
| Br(2)–Cd(1)–O(1) | 86.61(9) | O(11)–Cu(2)–O(21) | 78.4(1) |
| Br(2)–Cd(1)–O(21) | 84.41(7) | O(11)–Cu(2)–N(14) | 84.8(2) |
| Br(3)–Cd(1)–O(1) | 91.4(1) | O(11)–Cu(2)–N(24) | 159.6(2) |
| Br(3)–Cd(1)–O(21) | 98.89(9) | O(21)–Cu(2)–N(24) | 86.5(2) |
| Br(1)–Cd(1)–Br(2) | 125.03(3) | N(14)–Cu(2)–O(21) | 162.6(1) |
| Br(1)–Cd(1)–Br(3) | 114.68(2) | N(14)–Cu(2)–N(24) | 108.8(2) |
| Br(2)–Cd(1)–Br(3) | 120.29(2) | Br(2)–Cu(2)–O(11) | 97.0(1) |
| O(11)–Cu(1)–O(21) | 77.8(1) | Br(2)–Cu(2)–O(21) | 89.3(1) |
| O(11)–Cu(1)–O(21a) | 102.2(1) | Br(2)–Cu(2)–N(14) | 97.0(1) |
| O(11)–Cu(1)–Br(1a) | 92.1(1) | Br(2)–Cu(2)–N(24) | 96.4(1) |

[a] Symmetry transformation used to generate equivalent atoms: $-x + 1/2, -y + 3/2, -z + 1$.

basal positions at average distances of 1.947(3) (for Cu–O) and 2.080(5) Å (for Cu–N). The coordination is completed by the bridging bromide anion, Br(2), at 2.8300(9) Å. Five-coordination of each cadmium atom is completed by three bromide anions [average 2.5870(9) Å] and two oxygen atoms [from the dmso molecule and $\mu_2$-oxygen from the L group at 2.374(4) and 2.504(4) Å, respectively] in a compressed trigonal bipyramidal geometry. The O(1)–Cd–O(21) angle of 168.8(1)° shows that the trigonal bypiramid around cadmium is much less distorted comparing to that in **1**. The presence of the molecular inversion centre requires all five metal atoms to lie in the same plane. In the Cu–Cd–Cu–Cd parallelogram centred on the fifth Cu the bridged Cu ··· Cu and Cd ··· Cu separations are 2.8986(5) and 3.5128(9)–3.6206(5) Å, respectively.

### Description of the structure of 3

The hexanuclear complex, $[Cd_4Cu_2Cl_6L_6(H_2O)_2]$ **3**, is made up of two symmetry-related units with triangular $CuCd_2$ cores linked by amino alkoxo bridges, involving cadmium centres of both units (Fig. 3). Selected bond lengths and angles are listed in Table 4. Each L group adopts a chelating-bridging mode linking three metal atoms. The triangular planes formed by two cadmium and one copper atoms are capped on both sides by $\mu_3$-oxygen atoms from L groups. The two crystallographically independent cadmium centres have distinct chemical environments and both adopt distorted octahedral coordination geometries, $Cd(1)Cl_2O_4$ and $Cd(2)ClNO_3O_{(H2O)}$, with an average Cd–Cl distance of 2.525(1) and Cd–O/N bond lengths in the range 2.220(3)–2.655(3) Å. The copper atom adopts a square-pyramidal geometry with donor atoms of two L groups in the basal plane (average Cu–O and Cu–N distances of 1.942(3) and 2.051(4) Å, respectively) and an elongated apical bond to Cl(1) [2.767(1) Å]. The intermetallic distances in **3** range from 3.1312(7)–3.1379(6) (Cd ··· Cu) to 3.3995(6)–4.0435(6) Å (Cd ··· Cd).

**Table 4** Selected bond distances (Å) and angles (°) for **3**[a]

| | | | |
|---|---|---|---|
| Cd(1)–O(11) | 2.655(3) | Cd(2)–O(01) | 2.292(4) |
| Cd(1)–O(21) | 2.330(2) | Cd(2)–Cl(3) | 2.515(1) |
| Cd(1)–O(31) | 2.318(2) | Cd(2)–N(34) | 2.284(3) |
| Cd(1)–O(31a) | 2.250(2) | Cu(1)–O(11) | 1.939(3) |
| Cd(1)–Cl(1) | 2.561(1) | Cu(1)–O(21) | 1.945(2) |
| Cd(1)–Cl(2) | 2.499(1) | Cu(1)–Cl(1) | 2.767(1) |
| Cd(2)–O(11) | 2.220(3) | Cu(1)–N(14) | 2.056(4) |
| Cd(2)–O(21) | 2.462(2) | Cu(1)–N(24) | 2.046(3) |
| Cd(2)–O(31) | 2.296(2) | | |
| | | | |
| O(11)–Cd(1)–O(21) | 60.72(8) | O(21)–Cd(2)–O(01) | 155.9(1) |
| O(11)–Cd(1)–O(31) | 75.44(8) | O(21)–Cd(2)–N(34) | 103.3(1) |
| O(11)–Cd(1)–O(31a) | 96.05(8) | Cl(3)–Cd(2)–O(11) | 96.58(7) |
| O(21)–Cd(1)–O(31) | 79.12(8) | Cl(3)–Cd(2)–O(21) | 88.54(6) |
| O(21)–Cd(1)–O(31a) | 153.49(8) | Cl(3)–Cd(2)–O(31) | 163.14(6) |
| O(31)–Cd(1)–O(31a) | 82.82(8) | Cl(3)–Cd(2)–O(01) | 98.53(9) |
| Cl(1)–Cd(1)–O(11) | 75.56(6) | Cl(3)–Cd(2)–N(34) | 96.12(8) |
| Cl(1)–Cd(1)–O(21) | 88.13(6) | O(31)–Cd(2)–N(34) | 79.4(1) |
| Cl(1)–Cd(1)–O(31) | 150.95(6) | O(31)–Cd(2)–O(01) | 98.2(1) |
| Cl(1)–Cd(1)–O(31a) | 98.70(6) | N(34)–Cd(2)–O(01) | 98.8(1) |
| Cl(1)–Cd(1)–Cl(2) | 103.99(3) | O(11)–Cu(1)–O(21) | 81.5(1) |
| Cl(2)–Cd(1)–O(11) | 155.89(6) | Cl(1)–Cu(1)–O(11) | 83.57(8) |
| Cl(2)–Cd(1)–O(21) | 95.22(6) | Cl(1)–Cu(1)–O(21) | 90.85(8) |
| Cl(2)–Cd(1)–O(31) | 103.09(6) | Cl(1)–Cu(1)–N(14) | 101.6(1) |
| Cl(2)–Cd(1)–O(31a) | 107.72(6) | Cl(1)–Cu(1)–N(24) | 93.61(9) |
| O(11)–Cd(2)–N(34) | 162.6(1) | O(11)–Cu(1)–N(14) | 86.9(1) |
| O(11)–Cd(2)–O(21) | 65.32(9) | O(11)–Cu(1)–N(24) | 167.1(1) |
| O(11)–Cd(2)–O(31) | 85.08(9) | N(14)–Cu(1)–O(21) | 162.0(1) |
| O(11)–Cd(2)–O(01) | 90.9(1) | N(14)–Cu(1)–N(24) | 106.0(1) |
| O(21)–Cd(2)–O(31) | 76.87(8) | O(21)–Cu(1)–N(24) | 85.9(1) |

[a] Symmetry transformation used to generate equivalent atoms: $1 - x, 1 - y, -z$.

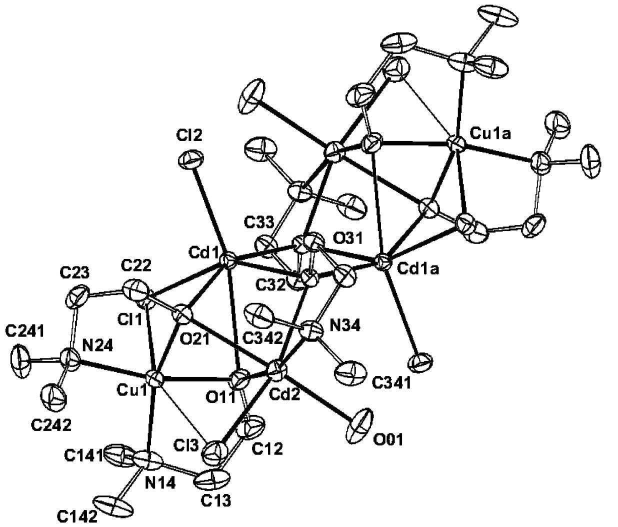

**Fig. 3** Molecular structure of complex **3**, showing the atom numbering, with 50% probability displacement ellipsoids.

## Conclusion

A convenient synthetic route employing zerovalent metal as the source of one of the metals in the synthesis of heterometallic complexes has been confirmed and extended. The reactions of copper powder with cadmium halides and 2-dimethylaminoethanol, in dmso, resulted in formation of three novel, polynuclear Cd/Cu complexes with unprecedented molecular structures. The subtle interactions that control the formation of complexes under such reaction conditions and their architectural characteristics may be rationalized after the event, but can rarely be predicted in advance. Obviously for these three systems, a key difference lies in the nature of the $X^-$ anion. Therefore, it can be inferred that the type of the counterion is of crucial importance in determining the nuclearity and structure of the Cd/Cu complexes formed, in contrast to the analogous Cu/Zn compounds.[5] A point to note is that in the Cd/Cu complexes there are no terminal bonds formed between the Cu centres and any of the halides, unlike the bonding pattern in the Cu/Zn systems. The bromide-containing **2** and chloride-containing **3** complexes do have halides bridging between Cu and Cd centres, but the iodide-containing complex **1** has only terminal Cd–I bonds. The observed structures may then, perhaps, relate back to the thermodynamic properties of the cadmium halide precursors. Overall, these results demonstrate significant structural flexibility of heterometallic cores made up of Cu, Cd, halide ions with O atoms from 2-dimethylaminoethanol so that a smaller anion induces a structure of higher nuclearity.

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