A Facile Direct Synthesis of Bimetallic $Cu^{II}Zn^{II}$ Complexes with Ethylenediamine Revealing Different Types of Chain Crystal Structures

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Unactivated copper metal powder and zinc oxide readily react with ethylenediamine (en) in nonaqueous [methanol, dimethylformamide (dmf), dimethyl sulfoxide (dmso), acetonitrile] solutions of ammonium salts under ambient conditions producing, in high yields, a series of heterobimetallic complexes of general formula $[Cu(en)_2ZnX_4]\cdot(Solv)$, where X = Cl, Br, NCS, CH_3COO (OAc); Solv = dmf, dmso, CH_3CN, H_2O. The single-crystal X-ray analysis of the complexes reveals chain structures, which are based on the completion of the octahedral coordination of Cu^{II} by two bridging X atoms from ZnX_4^{2-}. The ZnX_4^{2-} is shown to be a distorted tetrahedron (Cl, Br, NCS) or a very distorted octahedron (OAc) and to behave as a one- or two-linking centre bridging ligand. The chains are found to be zigzag $[Cu(en)_2ZnCl_4]\cdot dmso$ (**1**), $[Cu(en)_2ZnCl_4]\cdot dmf$ (**2**), $[Cu(en)_2Zn(NCS)_4]\cdot CH_3CN$ (**3**), quasi linear $[Cu(en)_2Zn(OAc)_4]$ (**4**), or helical, $[Cu(en)_2Zn(NCS)_4]\cdot 0.5H_2O$ (**5**), depending on the nature of the anion and solvent. Complex **4** represents the first compound containing $Zn(OAc)_4^{2-}$ to be crystallographically authenticated.

Introduction

The one-pot synthesis of metal complexes using elemental metals as starting materials, the so called "direct synthesis of coordination compounds" (DS),[1] has become an active research field and is undergoing rapid progress. Among the various methods of DS — cryosynthesis, electrochemical synthesis, mechanosynthesis — the oxidative dissolution of unactivated coarse-grain metal powders in solutions of ligands is one of the most important because of its simplicity and versatility. This method has provided a route to the synthesis of almost all the main types of monometal coordination compounds.[1,2]

Recently we have expanded this approach to the preparation of mixed-metal complexes that are of current interest due to their promising physical and biological properties. The synthetic procedure shown in Scheme 1 has been used to produce a series of new heterobimetallic Cu^{II}/M^{II} (M = Co, Ni, Zn, Pb) complexes with amino alcohols (HL).[2−8]

$$Cu^0 - M^0/MX_2 \text{ - HL - Solv (in air)}$$

Scheme 1

The synthetic route (Scheme 1) is effective when using proton-donating ligands. In this paper we suggest developing DS for the use of aprotic ligands (L). The essence of the proposed approach is to use ammonium salts as both proton- and anion-donating reagents (Scheme 2).

$$Cu^0 \text{ - } M^0/MO \text{ - L - } NH_4X \text{ - Solv (in air)}$$

Scheme 2

Ethylenediamine was employed in our synthesis as an aprotic ligand. It has been shown that ethylenediamine can take part in the activation of the metal surface and also in electron transfer in the reacting system.[9] Moreover, it is a strong coordinating agent that is efficiently applied in supramolecular design.[10−13]

Exploiting this approach (Scheme 2), we have synthesized a number of $Cu^{II}Zn^{II}$ complexes with ethylenediamine, which have the general formula $[Cu(en)_2ZnX_4]\cdot n\,Solv$ (X = Cl, Br, SCN, OAc; Solv = dmf, dmso, CH_3CN, and H_2O which is produced in the reaction; $n = 0, 0.5, 1$). The reactions proceed in the following way:

$$Cu^0 + ZnO + 2\,en + 4\,NH_4X + 1/2\,O_2 + n\,Solv \rightarrow [Cu(en)_2ZnX_4]\cdot n\,Solv + 4\,NH_3 + 2\,H_2O$$

In each case the reactions were conducted in air, at 50−60 °C and with stirring for 1−2 h. The yields of the products were up to 90%.

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Details of the syntheses, crystal structures and IR spectroscopic investigations of the complexes are reported.

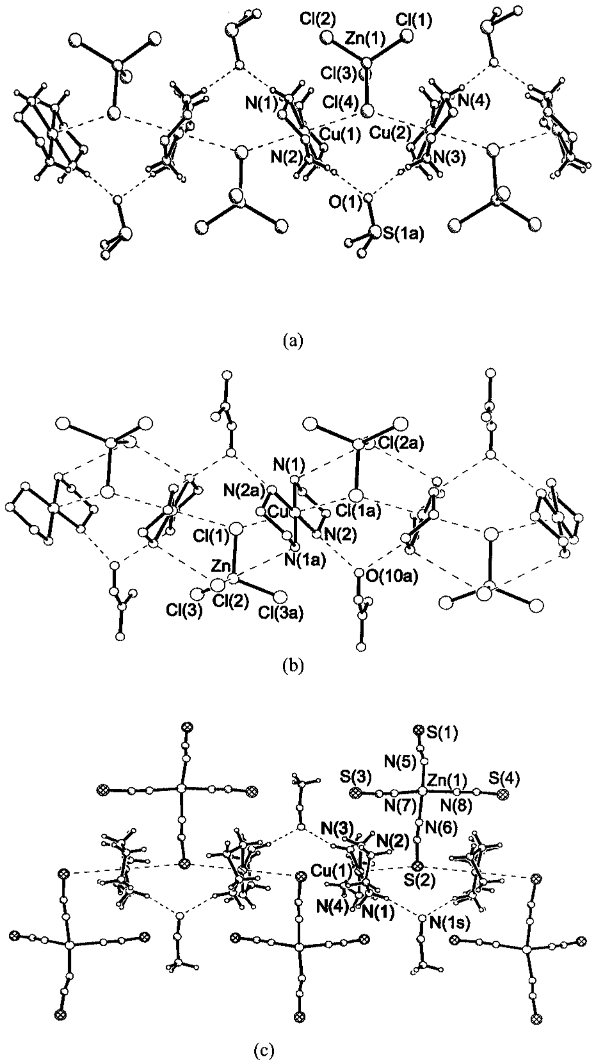
Results and Discussion

Zigzag CuZn Chain Structures of [Cu(en)$_2$ZnCl$_4$]·dmso (1), [Cu(en)$_2$ZnCl$_4$]·dmf (2), and [Cu(en)$_2$Zn(NCS)$_4$]·CH$_3$CN (3)

All the titled complexes possess the same type of crystal structure. The tetrahedral ZnX$_4^{2-}$ anions behave as one-linking centre bridging ligands, spanning the square planar Cu(en)$_2^{2+}$ cations in the *trans* positions with the Cl (in **1**, **2**) or S (in **3**) atoms, building up one-dimensional networks (Figure 1). The unusual coordination mode of ZnX$_4^{2-}$ in these complexes is most probably due to the set of hydrogen bonds (ca. 3.0−3.2 Å) between the amino groups of ethylenediamine and the donor atoms of the nonbridged X ligands. Usually, the coordination is two-linking for similar complexes, as in [ZnL$_2$][ZnCl$_4$] (L = diacetone alcohol).[14] Additionally the structure is supported by the guest dimethyl sulfoxide, dimethylformamide or acetonitrile molecules accommodated in the interchain space and hydrogen bonded through the O (dmso, dmf) or N (CH$_3$CN) atoms to the NH$_2$ groups (Figure 1). The lengths of the en-solvate hydrogen bonds show the strongest connection in case of dmso molecule [*d*(N···O$_{dmso}$) are 2.95(1) and 2.94(1) Å (**1**), *d*(N···O$_{dmf}$) are 3.171(7) and 2.973(8) Å (**2**), *d*(N···N) are 3.13(2) and 3.07(2) Å (**3**)].

The chains of Cu−Zn atoms have a zigzag shape with the Cu−Zn−Cu angle [89.06(2)° (**1**), 82.88(2)° (**2**), 66.05(3)° (**3**)] being dependant on both the nature of the X ligands in the ZnX$_4^{2-}$ anion and the nature of the solvate molecule. The Cu···Cu distances within the chains are 5.910(1), 5.5130(5) and 6.308(3) Å for **1**, **2** and **3**, respectively.

Bond lengths in the en ligands and Cu−N distances (Table 2) are in accordance with those found in the literature for similar copper(II) complexes.[15,16] The axial Cu−X distances are 3.117(3) and 3.085(4) Å (Cu−Cl, **1**), 2.9285(8) Å (Cu−Cl, **2**), 3.202(4) Å and 3.232(4) Å (Cu−S, **3**). These are quite long but do occur in complexes that have an elongated tetragonal or rhombic octahedral stereochemistry of the copper(II) ion, e.g. the Cu−Cl$_{ax}$ distances of ca. 3.0−3.2 Å are found in Cs$_3$[Cu$_2$Cl$_7$(H$_2$O)$_2$],[17] (Me$_3$NH)$_2$[Cu$_4$Cl$_{10}$],[18] [Pt(NH$_3$)$_4$CuCl$_4$],[19] and the Cu−S$_{ax}$ of 3.00 and 3.27 Å in [Cu(NH$_3$)$_4$(SCN)$_2$][20] and [Cu(en)$_2$(SCN)$_2$],[21] respectively. The geometrical parameters of ZnX$_4^{2-}$, namely nonequivalence of the Zn−Cl and Zn−N bond lengths (Table 2), lend additional support to the conclusion that the complex anions are weakly or *semi*-coordinated[22] to the copper(II) ion and not just positioned by van der Waals forces.



(a)

(b)

(c)

Figure 1. Structures of zigzag CuZn chains in (a) [Cu(en)$_2$ZnCl$_4$]·dmso (**1**), (b) [Cu(en)$_2$ZnCl$_4$]·dmf (**2**), (c) [Cu(en)$_2$Zn(NCS)$_4$]·CH$_3$CN (**3**), with atomic numbering

Quasi Linear CuZn Chain Structure of [Cu(en)$_2$Zn(OAc)$_4$] (4)

Although the main building blocks of the acetate complex Cu(en)$_2^{2+}$ and Zn(OAc)$_4^{2-}$ show a formal resemblance to **1−3,** the differences in their crystal structures are quite significant. Most importantly, the Zn atom in the tetraacetatozincate ion is not four- but now six-coordinate through two asymmetrically chelating and two monatomic bridging bidentate acetate groups (Figure 2). The octahedron ZnO$_6$ is very distorted: the Zn−O distances and O−Zn−O angles vary from 2.00−2.41 Å and 57.0−154.4°, respectively (Table 2). Because no crystallographic data was found for Zn(OAc)$_4^{2-}$ a structural comparison was made with M(OAc)$_4^{2-}$ (M = Cu, Cd)[23] and Zn(NO$_3$)$_4^{2-}$.[24] In these complexes the symmetry of the resulting coordination polyhedron is approximately D_{2d} and depicted as a distorted dodecahedron. The differences in the bond lengths M−O within a chelate carboxylate group or nitrate ring are very significant [Cu−O(OAc) = 1.97−2.79 Å and Zn−O(NO$_3$) = 2.03−2.52 Å]. In the case of the tetranitratozincate complex the distortions observed were explained by the tendency of the Zn^{II} ion to undergo tetrahedral coordination; this explanation may also be applicable in our case.

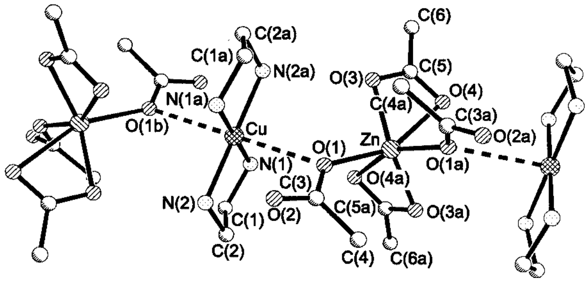


Figure 2. Structure of quasi linear CuZn chain in $[Cu(en)_2Zn(OAc)_4]$ (**4**) with atomic numbering.

It is worth noting that the absence of data on the crystal structure of $Zn(OAc)_4{}^{2-}$ may not be accidental but due to its low thermodynamic stability. A search for isomorphous crystals of $CaCu(OAc)_4{\cdot}6H_2O$ was undertaken by Langs and Hare,[23] but all attempts to substitute the Zn atoms for Cu atoms were met with failure. The existence of the $Zn(OAc)_4{}^{2-}$ in **4** is presumably stabilized by the $Cu(en)_2{}^{2+}$ cation, which is apt to the formation of numerous hydrogen bonds. Indeed, all the acetate oxygen atoms [except O(1), which is bridging the Cu and Zn atoms] take part in hydrogen bonding (Table 3).

The arrangement of the Cu and Zn atoms is almost linear, with the angle at the Cu atom (on an inversion centre) being 180° and that at the Zn atom, 170.25(2)°. The Cu···Zn distances are 4.1064(7) Å.

Helical CuZn Chain Structure of $[Cu(en)_2Zn(NCS)_4]{\cdot}0.5H_2O$ (5)

One of the more interesting structures is given in Figure 3 where a helical type of chain crystal structure is presented. A comparison of the structures of **3** and **5** demonstrates seemingly insignificant changes in composition, such as the replacement of an included acetonitrile molecule for a water molecule, associated with dramatic changes in the supramolecular structure. In contrast to **3**, in the hydrate complex a $Zn(NCS)_4{}^{2-}$ ion acts as a two-linking centre bridging ligand connecting the $Cu(en)_2{}^{2+}$ moieties in an infinite bimetallic spiral. The spirals, running along the *a* axis, form channels filled with uncoordinated water molecules (Figure 3, see b).

The Zn^{II} coordination environment closely approximates tetrahedral symmetry, the N−Zn−N bond angle being 107−112°. The thiocyanato groups are almost linear with a mean value of the N−C−S angles of 177(2)°. The Zn−N−C linkages are bent with angles varying from 159(1)° to 177(2)°; those with maximal deviations from linearity have the NCS^- groups bridging Zn and Cu atoms with the minimal values being those of the N(6)C(6)S(2) group, which bridges the Zn atoms such that the Zn-NCS···Zn′ atoms are essentially linear [the S(2)···Zn distance and C(6)S(2)Zn angle are ca. 3.64 Å and 171° respectively] (Figure 3, see a). The S−C average distance of 1.62(2) Å, and C−N average distances of 1.14(2) Å are in accordance with the values observed in other thiocyanato-containing metal complexes.[25,26]

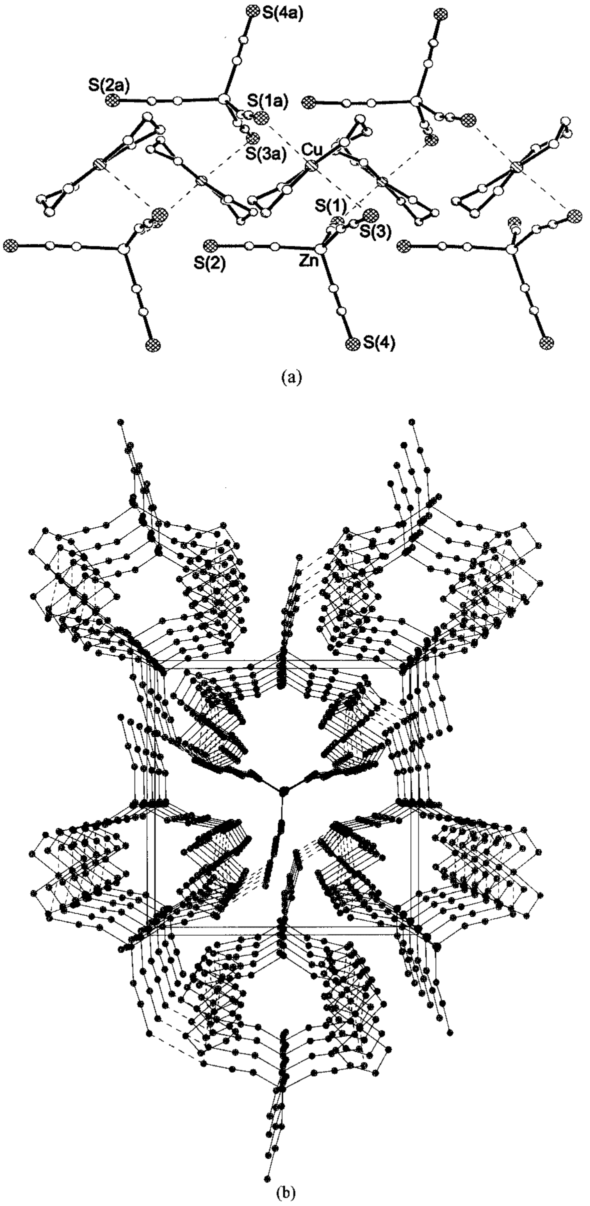


Figure 3. (a) Structure of helical CuZn chain in $[Cu(en)_2Zn(NCS)_4]{\cdot}0.5H_2O$ (**5**) with atomic numbering; (b) packing diagram of **5** revealing the channels down the a axis; hydrogen atoms and water molecules are omitted for clarity.

The Cu^{II} ion has asymmetric (4+1+1) surroundings; the axial positions are occupied by the S(1) and S(3) atoms from the thiocyanate groups: Cu−S(1) = 2.921(6) and Cu−S(3) = 3.218(5) Å; the S(1)−Cu−S(3) angle is 170.7(1)°. The CuN_4 fragment is largely planar and its geometrical parameters are consistent with those normally observed.[16]

IR Spectroscopic Measurements

The infrared spectra for complexes **1−5** contain characteristic ν(N−H), ν(C−H), δ(HNH), ν(C−N) and ν(C−C) frequencies for ethylenediamine in the ranges 3325−3130, 2990−2890, 1605−1580 (in **4** the corresponding mode of en is obscured by stretching vibrations of the carboxylate group), 1105−1053 and 990−980 cm^{-1}, respectively. Evidence for the coordination of en is provided by the shift of asymmetrical and symmetrical NH stretching frequencies of ca. 30−100 cm^{-1} to lower values and CH stretching frequencies of ca. 50−80 cm^{-1} to higher values compared with corresponding ones for en itself [3355, 3270 cm^{-1} − ν(NH); 2925, 2855 cm^{-1} − ν(CH)].[27,28] Two strong and broad absorption bands found for the acetate groups in complex **4** (1630− 580 and 1430−1390 cm^{-1}) lead to the Δ value [$\Delta = \nu_{as}(COO) - \nu_s(COO)$] in the range 150−240 cm^{-1}. This value is consistent with bridging unidentate or asymmetrical chelate ("pseudo-unidentate") carboxylate coordination.[29] The coordinated thiocyanate groups in **3** and **5** are confirmed by the presence of the intense absorption at 2090 cm^{-1} attributed to ν_{as}(C≡N) and the weak ν(CS) absorption at 835 cm^{-1}.[26] The presence of the solvate molecules in **1**−**3** can be identified by the peaks at 1020 and 950 cm^{-1} (for dmso, **1**), 1650 cm^{-1} (for dmf, **2**), and 2250 cm^{-1} (for CH_3CN, **3**). It should be noted that the peaks of ν(SO) and ν(CO) found in **1** and **2** are typical for coordinated dmso and dmf[26] but in our case the shift of the frequencies to lower values can be explained by the participation of the solvates in hydrogen bonding.

Conclusion

This paper describes a novel synthetic method for the preparation of bimetallic Cu/Zn complexes with ethylenediamine using zerovalent copper in powdered form. We consider that such an approach can also be used for the synthesis of other mixed-metal compounds, e.g. Cu/Cd, Cu/Ni and Cu/Co, with ethylenediamine or related ligands (diethylenetriamine, triethylenetetramine). Further work in this direction is in progress and will be presented in subsequent papers.

Experimental Section

General: All chemicals were of reagent grade and used as received, all experiments were carried out in air. Elemental analyses for

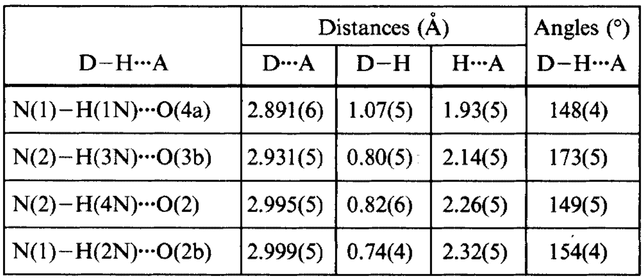
Table 1. Crystal data and structure refinement for **1**−**5**

	1	**2**	**3**	**4**	**5**
Crystal parameters:					
Empirical formula	$C_6H_{22}Cl_4CuN_4OSZn$	$C_7H_{23}Cl_4CuN_5OZn$	$C_{10}H_{19}CuN_9S_4Zn$	$C_{12}H_{28}CuN_4O_8Zn$	$C_8H_{17}CuN_8O_{0.5}S_4Zn$
Formula mass	469.05	464.04	522.49	485.29	490.47
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorombic
Space group	$P2_1/c$	$P2_1/m$	$P2_1$	$C2/c$	$P2_12_12_1$
a/Å	11.820(2)	8.407(1)	9.496(3)	14.213(3)	8.293(3)
b/Å	8.247(2)	11.026(1)	12.615(3)	14.840(3)	15.267(6)
c/Å	18.169(4)	9.429(1)	9.859(3)	9.334(2)	15.573(3)
α/°	90	90	90	90	90
β/°	94.33(3)	96.856(2)	115.45(3)	94.60(3)	90
γ/°	90	90	90	90	90
V/Å^3	1766.1(7)	867.8(2)	1066.4(5)	1962.4(7)	1971.7(11)
Z	4	2	2	4	4
$D_{calcd.}$/g·cm^{-3}	1.764	1.776	1.627	1.643	1.649
μ/mm^{-1}	3.28	3.22	2.526	3.257	2.727
$F(000)$	948	470	530	1004	988
Data collection:					
Diffractometer	CAD-4	Siemens SMART	Siemens P3/PC	CAD-4	Siemens P3/PC
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Cu-K_α (λ = 1.54178 Å)	Mo-K_α (λ = 0.71073 Å)
T/K	293(2)	150	293(2)	293(2)	293(2)
2θ scan range /°	2.25−24.97	2−26.4	2.29−30.07	4.31−59.94	2.78−25.07
h, k, l ranges	+12, +9, ±21	±10, +13, +11	+13, +17, ±13	±15, +16, +10	+9, +18, +18
Reflections collected	3218	8636	2831	1559	1905
Independent reflections [R_{int}]	2977 [0.013]	1873[0.089]	2526[0.0634]	1456 [0.0239]	1905
Refinement:					
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.053$ $wR2 = 0.073(F)$	$R1 = 0.061$ $wR2 = 0.068(F)$	$R1 = 0.0734$ $wR2 = 0.1723$	$R1 = 0.0480$ $wR2 = 0.1233$	$R1 = 0.0623$ $wR2 = 0.1473$
R indices (all data)	$R1 = 0.088$ $wR2 = 0.085$	$R1 = 0.071$ $wR2 = 0.076$	$R1 = 0.0958$ $wR2 = 0.1838$	$R1 = 0.0562$ $wR2 = 0.1352$	$R1 = 0.1141$ $wR2 = 0.1721$
G.O.F. (F^2)	1.042(F)	1.649(F)	1.036	1.027	1.006
Δ(ρ)/e· Å^{-3}	+1.07, −0.95	+1.973, −1.206	+0.923, −0.730	+0.658, −0.990	+0.998, −0.580

Table 2. Selected bond lengths (Å) and angles (°) around metal atoms for **1**−**5** (symmetry transformations used to generate equivalent atoms: **1** *a* < −*x*, −*y*, −*z* >, *b* < 1 −*x*, −*y*, −*z* >; **2** *a* < *x*, 1/2 − *y*, *z* >; **4** *a* < −*x* + 1, *y*, −*z* + 1/2>, *b* < −*x* + 1/2, −*y* + 1/2, −*z* >)

1					
Cu(1)−N(1)	1.981(8)	N(1)−Cu(1)−N(2)	84.7(3)	Cl(1)−Zn(1)−Cl(2)	113.01(9)
Cu(1)−N(2)	2.013(8)	N(1)−Cu(1)−N(1a)	180.0	Cl(1)−Zn(1)−Cl(3)	109.9(1)
Cu(2)−N(3)	1.993(8)	N(1)−Cu(1)−N(2a)	95.3(3)	Cl(1)−Zn(1)−Cl(4)	109.2(1)
Cu(2)−N(4)	1.985(7)	N(2)−Cu(1)−N(2a)	180.0	Cl(2)−Zn(1)−Cl(3)	109.8(1)
Zn(1)−Cl(1)	2.246(3)	N(3)−Cu(2)−N(4)	85.0(3)	Cl(2)−Zn(1)−Cl(4)	108.3(1)
Zn(1)−Cl(2)	2.242(3)	N(3)−Cu(2)−N(3b)	180.0	Cl(3)−Zn(1)−Cl(4)	106.40(9)
Zn(1)−Cl(3)	2.271(3)	N(4)−Cu(2)−N(3b)	95.0(3)		
Zn(1)−Cl(4)	2.302(3)	N(4)−Cu(2)−N(4b)	180.0		
2					
Cu−N(1)	2.021(6)	N(1)−Cu−N(2)	85.2(2)	Cl(1)−Zn−Cl(2)	101.7(1)
Cu−N(2)	2.008(6)	Cl(1)−Cu−N(1)	85.5(2)	Cl(1)−Zn−Cl(3)	109.13(6)
Zn−Cl(1)	2.318(3)	Cl(1)−Cu−N(2)	89.6(2)	Cl(2)−Zn−Cl(3)	110.69(6)
Zn−Cl(2)	2.278(3)			Cl(3)−Zn−Cl(3a)	114.74(8)
Zn−Cl(3)	2.250(2)				
3					
Cu(1)−N(1)	1.918(10)	N(1)−Cu(1)−N(2)	84.8(5)	N(5)−Zn(1)−N(6)	122.9(3)
Cu(1)−N(2)	2.085(9)	N(1)−Cu(1)−N(3)	177.6(5)	N(5)−Zn(1)−N(7)	114.2(5)
Cu(1)−N(3)	2.085(8)	N(1)−Cu(1)−N(4)	94.3(4)	N(5)−Zn(1)−N(8)	103.6(5)
Cu(1)−N(4)	1.990(8)	N(2)−Cu(1)−N(3)	96.9(4)	N(6)−Zn(1)−N(7)	99.8(5)
Zn(1)−N(5)	1.949(8)	N(2)−Cu(1)−N(4)	178.1(5)	N(6)−Zn(1)−N(8)	105.7(5)
Zn(1)−N(6)	2.000(7)	N(3)−Cu(1)−N(4)	84.0(3)	N(7)−Zn(1)−N(8)	110.3(4)
Zn(1)−N(7)	1.886(12)				
Zn(1)−N(8)	2.043(11)				
4					
Cu−N(1)	1.995(4)	N(1)−Cu−N(2)	84.7(2)	O(1)−Zn−O(4a)	90.89(13)
Cu−N(2)	2.010(4)	N(1)−Cu−N(1a)	180.0	O(3)−Zn−O(4)	57.02(12)
Zn−O(1)	2.003(3)	N(1)−Cu−N(2a)	95.3(2)	O(3)−Zn−O(1a)	108.58(11)
Zn−O(3)	2.054(3)	N(2)−Cu−N(2a)	180.0	O(3)−Zn−O(3a)	136.9(2)
Zn−O(4)	2.410(4)	O(1)−Zn−O(3)	97.90(11)	O(3)−Zn−O(4a)	90.10(13)
		O(1)−Zn−O(4)	154.42(11)	O(4)−Zn−O(4a)	84.7(2)
		O(1)−Zn−O(1a)	103.2(2)	O(1)−Cu−O(1b)	180.0
5					
Cu(1)−N(1)	2.04(1)	N(1)−Cu(1)−N(2)	96.8(5)	N(5)−Zn(1)−N(6)	107.0(7)
Cu(1)−N(2)	2.02(1)	N(1)−Cu(1)−N(3)	178.7(5)	N(5)−Zn(1)−N(7)	109.4(5)
Cu(1)−N(3)	1.99(1)	N(1)−Cu(1)−N(4)	84.4(5)	N(5)−Zn(1)−N(8)	112.3(6)
Cu(1)−N(4)	1.99(1)	N(2)−Cu(1)−N(3)	84.5(5)	N(6)−Zn(1)−N(7)	108.1(7)
Zn(1)−N(5)	2.01(1)	N(2)−Cu(1)−N(4)	175.3(5)	N(6)−Zn(1)−N(8)	109.5(6)
Zn(1)−N(6)	1.96(1)	N(3)−Cu(1)−N(4)	94.3(6)	N(7)−Zn(1)−N(8)	110.3(6)
Zn(1)−N(7)	1.95(1)				
Zn(1)−N(8)	1.93(1)				

Table 3. Hydrogen bond parameters for **4** (symmetry operations: *a* <1 − *x*,*y*, 1/2 − *z*>, *b* <1/2 − *x*, 1/2 − *y*, − *z*>)



D−H···A	Distances (Å)			Angles (°)
	D···A	D−H	H···A	D−H···A
N(1)−H(1N)···O(4a)	2.891(6)	1.07(5)	1.93(5)	148(4)
N(2)−H(3N)···O(3b)	2.931(5)	0.80(5)	2.14(5)	173(5)
N(2)−H(4N)···O(2)	2.995(5)	0.82(6)	2.26(5)	149(5)
N(1)−H(2N)···O(2b)	2.999(5)	0.74(4)	2.32(5)	154(4)

metals were performed by atomic absorption spectroscopy, by standard titrimetric methods for anions and with a Carlo Erba Strumentazion Analyser (for C, H and N). Thermogravimetric analyses (TGA) were performed on polycrystalline samples *ca.* 150 mg in air at a scan speed of 10 °C/min on a derivatograph "Q−1500". Infrared spectra were recorded with KBr discs and in Nujol mulls on a UR−10 spectrophotometer in the 4000−400 cm^{-1} region using conventional techniques.

[Cu(en)$_2$ZnCl$_4$]·dmso (1): Copper powder (0.32 g, 0.005 mol), zinc oxide (0.41 g, 0.005 mol), ammonium chloride (1.54 g, 0.02 mol), dmso (20 cm^3) and ethylenediamine (0.7 cm^3, 0.01 mol) were placed in a flask in the above order, heated to 60 °C and magnetically stirred until total dissolution of Cu^0 and ZnO was observed (110 minutes). The dark-violet crystals suitable for X-ray crystallography formed immediately after cooling the resulting solution. The crystals were filtered out and dried in vacuo at room temperature. Mass collected 2.1 g, yield 89%. $C_6H_{22}Cl_4CuN_4OSZn$ (469.05): calcd. C 15.36, H 4.74, N 11.95, Cu 13.55, Zn, 13.94, Cl 30.23; found C 15.2, H 4.63, N 11.9, Cu 13.9, Zn, 14.3, Cl 29.9. TGA results indicated that **1** exhibited a weight loss of 41.71% in the temperature range 170−340 °C (calcd. 42.28% for the loss of one dmso and two ethylenediamine molecules per formula unit). IR (cm^{-1}): $\tilde{\nu}$ = 3315 s, 3260 s, 3145 s, 2990 w, 2950 sh, 1605 s, 1580 m, 1450 w, 1285 w, 1185 m, 1090 s, 1045 vs, 1020 vs, 975 w, 950 s, 710 s, 540 m. The compound is soluble in water, dmso and dmf.

$[Cu(en)_2ZnCl_4]$·dmf (2): This complex was obtained in a similar manner to **1**, except for the use of dmf (20 cm^3) instead of dmso. Mass collected 1.9 g, yield 82%. $C_7H_{23}Cl_4CuN_5OZn$ (464.04): calcd. C 18.12, H 5.01, N 15.12, Cu 13.71, Zn, 14.11, Cl 30.60; found C 18.3, H 4.9, N 16.0, Cu 14.0, Zn, 13.5, Cl 29.2. TGA results showed an initial weight loss of 15.03% in the temperature range 110−190 °C (calcd. 15.75% for the loss of one dmf molecule per formula unit). IR (cm^{-1}): $\tilde{\nu}$ = 3310 s, 3260 s, 3160 w, 2980 w, 2895 w, 1650 vs, 1600 s, 1585 sh, 1455 w, 1410 w, 1385 m, 1325 w, 1285 w, 1250 w, 1095 m, 1045 vs, 975 w, 705 m, 660 w, 535w, 475w, 420w. The compound is soluble in water, dmso and dmf.

$[Cu(en)_2Zn(NCS)_4]\cdot CH_3CN$ (3): This complex was obtained in a similar manner to **1**, except for the use of NH_4NCS instead of NH_4Cl in CH_3CN (25 cm^3). Mass collected 1.62 g, yield 62%. $C_{10}H_{19}CuN_9S_4Zn$ (522.49): calcd. C 22.99, H 3.67, N 15.12, Cu 13.71, Zn14.11; NCS 50.14; found C 22.7, H 3.5, N 15.3, Cu 13.7, Zn, 13.7; NCS 49.9. TGA results showed a weight loss of 8.00% in the temperature range 50−130 °C (7.86% for the loss of one CH_3CN molecule per formula unit). IR (cm^{-1}): $\tilde{\nu}$ = 3325 m, 3270 m, 3235 m, 3155 w, 2955 w, 2890 w, 2250 w, 2090 vs, 1585 m, 1460 w, 1385 w, 1370 w, 1360 w, 1325 w, 1280 w, 1180−1150 br, 1095 m, 1045 s, 1010 w, 980 w, 880 w, 690 w, 535 w, 520 w, 480 w. The compound is insoluble in water but soluble in dmso and dmf.

$[Cu(en)_2Zn(CH_3COO)_4]$ (4): This complex was obtained in a similar manner to **1**, except for the use of CH_3COONH_4 instead of NH_4Cl. Mass collected 0.95 g, yield 39%. $C_{12}H_{28}CuN_4O_8Zn$ (485.29): calcd. C 29.69, H 5.83, N 11.55, Cu 13.09, Zn 13.47; found C 29.3, H 6.1, N 11.6, Cu 13.3; Zn, 13.5. TGA results showed an initial decomposition of **4** at 40 °C but no well-separated weight loss steps were observed. IR (cm^{-1}): $\tilde{\nu}$ = 3340−3305 br, 3275 sh, 3140 s, 2985−2955 br, 2900 w, 1625 sh, 1575 vs, 1425 vs, 1405 sh, 1340 m, 1280 w, 1185−1165 br, 1105 w, 1050 vs, 1020 m, 985 w, 915 m, 735 w, 660 s, 615 w, 550 w, 525 w, 480 w, 415 w. The compound is soluble in water, dmso and dmf.

$[Cu(en)_2Zn(NCS)_4]\cdot 0.5\ H_2O$ (5): This complex was obtained in a similar manner to **1**, except for the use of NH_4NCS instead of NH_4Cl in CH_3OH (25 cm^3). Mass collected 0.47 g, yield 19%. $C_8H_{17}CuN_8O_{0.5}S_4Zn$ (490.47): calcd. C 19.59, H 3.50, N 20.54, Cu 11.65, Zn 11.98; NCS 42.59; found C 20.1, H 3.4, N 21.5, Cu 11.5, Zn 12.2; NCS 39.5. The presence of water molecules in **5** is clearly indicated in the TGA results, which exhibited an initial weight loss of 1.99% in the temperature range 180−205 °C [calcd. 1.84% for the loss of half a water molecule per formula unit]. IR (cm^{-1}): $\tilde{\nu}$ = 3320 m, 3290 sh, 3230 m, 3130 w, 2980−2950 br, 2930 sh, 2885 w, 2090 vs, 1580 s, 1455 w, 1320 w, 1275 w, 1165 w, 1090 m, 1040 s, 1010 w, 980 w, 830 w, 690 m, 520 w, 475 w. The compound is insoluble in water and soluble in dmso and dmf.

X-ray Data Collection and Processing: Well-shaped crystals of **1−5** were suitable for X-ray analysis. Crystal data and details of structure solutions are summarized in Table 1 and selected bond lengths and angles in Table 2.

The data were corrected for Lorentz-polarisation effects and for the effects of absorption by the gausian for **1** and multiscan methods for **2**. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms (except those of the water molecule in **5**) were located in Fourier difference syntheses or assigned at geometrically calculated positions and refined using a riding model (**1**, **4**) or fixed (**2**, **3**, **5**). The structures were solved by direct methods and refined by full-matrix least-squares methods using the SHELXL−93, SHELXL-97[30−32] and XTAL3.4 programs.[33] For **1**, the dmso S atom and Me groups were modelled as being disordered over two sites.

CCDC-174059−174063 contains 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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