

# New One- and Two-Dimensional Heterometallic Cu/Cd Halogeno or Thiocyanato Bridged Coordination Polymers Synthesized Directly from Elemental Copper and Cadmium Oxide in the Presence of Ethylenediamine

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Z. Naturforsch. **58b**, 1117 – 1123 (2003); received June 2, 2003

Three heterometallic Cu/Cd complexes  $[\text{Cu}(\text{en})_2\text{CdBr}_4]\cdot\text{dmsO}$  (**1**),  $[\text{Cu}(\text{en})_2\text{CdI}_4]\cdot\text{dmf}$  (**2**) and  $[\{\text{Cu}(\text{en})_2\}_3\text{Cd}(\text{NCS})_6](\text{NCS})_2$  (**3**) have been synthesized by means of an open-air reaction of unactivated copper powder, cadmium oxide,  $\text{NH}_4\text{X}$  ( $\text{X} = \text{Br}, \text{I}, \text{NCS}$ ) and ethylenediamine in non-aqueous solvents, like dmsO, dmf and  $\text{CH}_3\text{OH}$ . The selection of a counter-anion in the initial ammonium salt provides a facile approach to the controlled assembly of one- or two-dimensional extended networks. Crystallographic investigations reveal that **1** and **2** possess 1D structures *via* semi-coordination ( $\text{Cu}^{2+} \dots \text{X}$ ) and hydrogen bonds ( $\text{NH}_2 \dots \text{O}_{\text{Solv}}$ ) forming chains with a zigzag arrangement of copper and cadmium atoms. In complex **3** the cadmium atom of each  $\text{Cd}(\text{NCS})_6^{4-}$  anionic block forms bridges with Cu(II) ions *via* the sulfur atoms of thiocyanate groups to give 2D polymeric sheets, featuring two different ring sizes, one a 32-membered ring  $[\text{Cu}_4\text{Cd}_4(\mu\text{-SCN-S}, N)_8]$  and the other a 16-membered ring  $[\text{Cu}_2\text{Cd}_2(\mu\text{-SCN-S}, N)_4]$ . It is noteworthy, that **3** shows a quite rare  $\text{Cd}(\text{NCS})_6^{4-}$  fragment with N-bonded thiocyanate groups.

**Key words:** Heterometallic Coordination Polymers, Elemental Copper, Cadmium Oxide, Ethylenediamine

## Introduction

The recent surge of research activity in the synthesis of coordination polymers which is based on multifunctional ligands has been motivated by the ability of metal-ligand coordination to provide a facile route to network architectures with a variety of topologies. An impressive diversity of one-, two- and three-dimensional frameworks containing different structural motifs has been reported to date [1]. The formation of the coordination networks was shown to depend upon several factors such as the mode of coordination by the metal atom, the selection of the ligand, the type of anion present, and the reaction conditions. Ethylenediamine binds well to metal centers, and has therefore been employed extensively in the construction of the

metal-organic parts in the role of an organic linker [2]. To use two dissimilar metals in the design of coordination compounds can potentially give rise to more complex physical properties and also to an even greater diversity of the polymeric structures. A large number of preparations have been offered in order to receive heterometallic complexes, but the use of polynucleating ligands and complexes is still one of major synthetic methods. We have previously shown that various metal complexes can be obtained easily through a "one-pot" reaction of a metal powder or metal oxide with a complex-forming agent in non-aqueous solution in air [3]. The approach to attach ethylenediamine to a metal center and construct a building block which is assembled into an infinite heterometallic structure with a second metal center resulted in a number of novel

Cu/Zn complexes with ethylenediamine of general formula  $[\text{Cu}(\text{en})_2\text{ZnX}_4] \cdot n\text{Solv}$  ( $\text{X} = \text{Cl}, \text{NCS}, \text{O}_2\text{CMe}$ ;  $\text{Solv} = \text{dmf}, \text{dmsO}, \text{CH}_3\text{CN}, \text{H}_2\text{O}$ ;  $n = 0, 0.5, 1$ ). Three types of 1D crystal structures – zigzag, quasi linear and helical – were found depending on the nature of the anion and the solvent [4]. In order to synthesize heterometallic complexes of higher dimensionality, we have replaced zinc by cadmium which is known to provide different geometries and coordination numbers [5]. Details of the synthesis and crystal structures as well as of spectroscopic data of **1**, **2** and **3** are reported.

## Experimental Section

**General:** 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 and by standard titrimetric methods for anions by the Department of Chemistry, National Taras Shevchenko University of Kyiv and with a Carlo Erba Strumentazion Analyzer (for C, H and N) by the Institute of Inorganic Chemistry, Vienna University of Technology.

### Synthesis of $[\text{Cu}(\text{en})_2\text{CdBr}_4] \cdot \text{dmsO}$ (**1**)

Copper powder (0.16 g, 0.0025 mol), CdO (0.32 g, 0.0025 mol),  $\text{NH}_4\text{Br}$  (0.98 g, 0.01 mol), dmsO (20  $\text{cm}^3$ ) and ethylenediamine (0.35  $\text{cm}^3$ , 0.005 mol) were heated to 50–60 °C and stirred magnetically until total dissolution of the copper metal and cadmium oxide was observed (30 min). The solution was filtered. Some three days after the addition of 15  $\text{cm}^3$  of isopropanol to the violet solution, violet crystals suitable for X-ray crystallography were formed. Crystals were separated by filtration, washed with dry isopropanol and finally dried *in vacuo* at r.t. Yield: 1.1 g, 63% (per copper). Analysis for  $\text{C}_6\text{H}_{22}\text{CuCdN}_4\text{OSBr}_4$  ( $M_r = 693.89$ ): calcd. C 10.39, H 3.20, N 8.07, Cu 9.16, Cd 16.20; found C 10.6, H 3.3, N 8.3, Cu 9.3, Cd 15.8. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3310 (br), 3260 (sh), 3230 (sh), 3140 (s), 2990 (w), 2960 (w), 1600 (s), 1580 (m), 1450 (w), 1285 (w), 1190 (w), 1180 (sh), 1100 (s), 1045 (vs), 1020 (vs), 980 (m), 955 (m), 710 (s), 540 (m), 530 (sh), 480 (w). The compound is soluble in water, dmsO and dmf.

### Synthesis of $[\text{Cu}(\text{en})_2\text{CdI}_4] \cdot \text{dmf}$ (**2**)

Copper powder (0.16 g, 0.0025 mol), CdO (0.32 g, 0.0025 mol),  $\text{NH}_4\text{I}$  (1.45 g, 0.01 mol), dmf (20  $\text{cm}^3$ ) and ethylenediamine (0.35  $\text{cm}^3$ , 0.005 mol) were heated to 50–60 °C and stirred magnetically until total dissolution of the copper metal and cadmium oxide was observed (15 min). The solution was filtered. Violet crystals suitable for X-ray crystallography separated 7 d after the addition of 15  $\text{cm}^3$

of isopropanol to the resulting solution. Crystals were filtered, washed with dry isopropanol and finally dried *in vacuo* at r.t. Yield: 1.7 g, 77% (per copper). Analysis for  $\text{C}_7\text{H}_{23}\text{CuCdN}_5\text{OI}_4$  ( $M_r = 876.86$ ): C 9.59, H 2.64, N 7.99, Cu 7.25, Cd 12.82; found C 9.8, H 2.8, N 8.3, Cu 6.9, Cd 12.5. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3295 (s), 3240 (s), 3145 (s), 2960 (w), 2940 (sh), 2900 (w), 1640 (vs), 1590 (s), 1490 (w), 1450 (m), 1440 (sh), 1410 (w), 1390 (m), 1320 (w), 1285 (w), 1260 (w), 1175 (m), 1095 (s), 1045 (vs), 1025 (m), 975 (m), 880 (w), 700 (m), 660 (m), 535 (s), 480 (w). The compound is soluble in water, dmsO and dmf.

### Synthesis of $[\{\text{Cu}(\text{en})_2\}_3\text{Cd}(\text{NCS})_6](\text{NCS})_2$ (**3**)

Copper powder (0.48 g, 0.0075 mol), CdO (0.32 g, 0.0025 mol),  $\text{NH}_4\text{NCS}$  (1.52 g, 0.02),  $\text{CH}_3\text{OH}$  (25  $\text{cm}^3$ ) and ethylenediamine (1.05  $\text{cm}^3$ , 0.015 mol) were heated to 50–60 °C and stirred magnetically until total dissolution of the copper metal and cadmium oxide was observed (90 min). The solution was filtered. Violet crystals suitable for X-ray crystallography separated 1 d after the addition of 15  $\text{cm}^3$  of isopropanol to the resulting violet solution. Crystals were filtered, washed with dry isopropanol and finally dried *in vacuo* at room temperature. The yield was 0.4 g, 14% (per copper, not optimized). Analysis for  $\text{C}_{20}\text{H}_{48}\text{Cu}_3\text{CdN}_{20}\text{S}_8$  ( $M_r = 1128.26$ ): calcd. C 21.29, H 4.29, N 24.83, Cu 16.90, Cd 9.96; found C 24.3, H 4.6, N 27.4, Cu 16.7, Cd 9.6. IR (KBr pellet and Nujol mulls,  $\text{cm}^{-1}$ ): 3320 (s), 3290 (sh), 3230 (s), 3130 (s), 2965 (w), 2905 (w), 2095 (vs), 2050 (vs), 1585 (s), 1460 (m), 1400 (w), 1320(w), 1285 (m), 1175 (w), 1100 (s), 1040 (vs), 1030 (sh), 980 (s), 950 (sh), 890 (w), 785 (w), 740 (w), 720 (s), 615 (w), 545 (m), 465 (m), 420 (w). The compound is insoluble in water and soluble in dmsO and dmf.

The complexes are stable in air for periods of months.

### Physical 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. UV/vis spectra were recorded on a Perkin Elmer 330 spectrophotometer using the diffuse-reflectance technique.

### Crystal structure determination

Well-shaped crystals of **1–3** 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.

Diffraction experiments were performed on a four-circle diffractometer “Siemens P3/PC” ( $\text{Mo-K}_\alpha$  radiation, graphite monochromator,  $2\theta/\theta$ -scan,  $\theta_{\text{max}} = 25^\circ$ ). Absorption was corrected for semi-empirically by means of  $\Psi$ -scan data. The structure was solved by direct method using the SHELXTL

Compound	1	2	3
Formula	C <sub>6</sub> H <sub>22</sub> CuCdN <sub>4</sub> OSBr <sub>4</sub>	C <sub>7</sub> H <sub>23</sub> CuCdN <sub>5</sub> OI <sub>4</sub>	C <sub>20</sub> H <sub>48</sub> Cu <sub>3</sub> CdN <sub>20</sub> S <sub>8</sub>
M	693.89	876.86	1128.26
Crystal system	orthorhombic	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>P</i> 1̄
<i>a</i> /Å	8.423(2)	8.739(2)	9.238(4)
<i>b</i> /Å	12.404(2)	12.408(3)	11.266(5)
<i>c</i> /Å	18.452(4)	10.156(3)	11.798(5)
$\alpha$ /°	90	90	98.66(3)
$\beta$ /°	90	95.01(2)	111.04(3)
$\gamma$ /°	90	90	103.39(3)
<i>V</i> /Å <sup>3</sup>	1927.8(7)	1097.2(5)	1077.2(8)
<i>Z</i>	4	2	2
<i>D</i> (calc)/g·cm <sup>−3</sup>	2.391	2.654	1.739
$\mu$ (Mo-K $\alpha$ )/mm <sup>−1</sup>	7.566	7.566	2.379
<i>F</i> (000)	1308	794	571
<i>h</i> , <i>k</i> , <i>l</i> Ranges	+10, +14, +21	−8+10, −2+14, $\pm$ 12	+11, $\pm$ 13, −14+13
Reflections collected	2243	2274	4229
Independent reflections	1893	1940	3641
<i>R</i> <sub>int</sub>	0.137	0.137	0.074
Final <i>R</i> indices			
[ <i>F</i> > 4 $\sigma$ ( <i>F</i> )] <i>R</i> 1	0.045	0.052	0.054
<i>R</i> <sub>1</sub> (all data)	0.110	0.063	0.087
<i>wR</i> <sub>2</sub> (all data)	0.106	0.138	0.145
G.O.F. ( <i>F</i> <sup>2</sup> )	0.917	0.986	1.009

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

<b>1</b>					
Cu(1)–N(1)	2.00(2)	N(1)–Cu(1)–N(2)	83.0(8)	Br(1)–Cd(1)–Br(2)	107.1(1)
Cu(1)–N(2)	2.02(1)	N(1)–Cu(1)–N(3)	179.5(7)	Br(1)–Cd(1)–Br(3)	116.6(1)
Cu(1)–N(3)	1.99(2)	N(1)–Cu(1)–N(4)	94.6(7)	Br(1)–Cd(1)–Br(4)	108.8(1)
Cu(1)–N(4)	2.01(1)	N(2)–Cu(1)–N(3)	96.7(7)	Br(2)–Cd(1)–Br(3)	107.7(1)
Cd(1)–Br(1)	2.549(2)	N(2)–Cu(1)–N(4)	177.1(8)	Br(2)–Cd(1)–Br(4)	107.1(1)
Cd(1)–Br(2)	2.612(2)	N(3)–Cu(1)–N(4)	85.7(7)	Br(3)–Cd(1)–Br(4)	109.1(1)
Cd(1)–Br(3)	2.554(2)				
Cd(1)–Br(4)	2.589(2)				
<b>2</b>					
Cu(1)–N(1)	2.002(8)	N(1)–Cu(1)–N(2)	85.4(4)	I(1)–Cd(1)–I(2)	100.78(5)
Cu(1)–N(2)	2.005(8)	N(1)–Cu(1)–N(2A)	94.6(4)	I(1)–Cd(1)–I(3)	107.48(3)
Cd(1)–I(1)	2.830(1)			I(2)–Cd(1)–I(3)	109.42(4)
Cd(1)–I(2)	2.289(2)			I(3)–Cd(1)–I(3A)	120.42(5)
Cd(1)–I(3)	2.730(1)				
<b>3</b>					
Cu(1)–N(1)	2.006(6)	N(1)–Cu(1)–N(2)	84.2(2)	N(7)–Cd(1)–N(8)	90.2(3)
Cu(1)–N(2)	1.995(6)	N(1)–Cu(1)–N(3)	178.0(3)	N(7)–Cd(1)–N(9)	94.4(2)
Cu(1)–N(3)	2.015(6)	N(1)–Cu(1)–N(4)	93.5(3)	N(8)–Cd(1)–N(9)	91.5(3)
Cu(1)–N(4)	1.998(6)	N(2)–Cu(1)–N(3)	97.8(3)		
Cu(2)–N(5)	2.019(6)	N(2)–Cu(1)–N(4)	174.8(2)		
Cu(2)–N(6)	2.044(6)	N(3)–Cu(1)–N(4)	84.5(3)		
Cd(1)–N(7)	2.348(7)	N(5)–Cu(2)–N(6)	83.8(2)		
Cd(1)–N(8)	2.306(8)				
Cd(1)–N(9)	2.312(7)				

\* Symmetry transformations used to generate equivalent atoms: **2** A (−*x* + 1, −*y* + 1, −*z* + 2).

Table 2. Selected bond lengths (Å) and angles (°) around metal atoms for **1–3**.\*

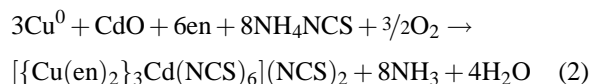
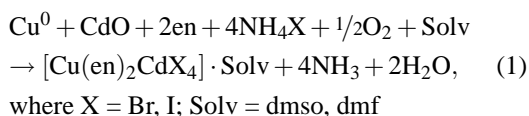
package [6]. Positions of the hydrogen atoms were located from the difference map of electron density and refined by a riding model with  $U_{\text{iso}} = nU_{\text{eq}}$  of the non-hydrogen atom bonded to the H-atom ( $n = 1.5$  for methyl and 1.2 for other H-atoms).

## Results and Discussion

### Synthesis and spectroscopic characterization

The reaction of copper powder, cadmium oxide and NH<sub>4</sub>X (X = Br, I, NCS) with ethylenediamine in dmsO,

dmf or CH<sub>3</sub>OH, in open air, gave microcrystals of **1** and **2** (in high yield) and complex **3** in low yield, according to eq. (1) for **1** and **2**, and eq. (2) for **3**. In each reaction, dioxygen is reduced.



The simultaneous presence of copper and cadmium in compounds **1**, **2**, and **3** was unambiguously determined by atomic absorption. The Cu to Cd ratio in the products correlates with the metal ratio in the initial mixture. The complexes **1** and **2** could also be isolated as the corresponding solvates from dmf in case **1**, and compounds of formula [Cu(en)<sub>2</sub>CdX<sub>4</sub>] from CH<sub>3</sub>OH and CH<sub>3</sub>CN solutions (X = Br) or dmsO, CH<sub>3</sub>OH and CH<sub>3</sub>CN solutions (X = I). It is noteworthy, that heterometallic compounds containing thiocyanate anions if formed could not be isolated from dmf, dmsO and acetonitrile solutions, probably because of the high solubility of the complexes in these solvents.

The structural features of three complexes were determined by IR and electronic spectroscopy and from single-crystal X-ray diffraction studies. The IR spectrum of all complexes in the range 4000–400 cm<sup>−1</sup> are quite similar and show all the characteristic ligand frequencies: ν(N–H), ν(C–H), δ(NH<sub>2</sub>), ν(C–N) and ν(C–C) in the ranges 3320–3295, 2990–2965, 1600–1585, 1045–1040 and 980–975 cm<sup>−1</sup>, respectively. In KBr disk, the infrared spectrum of **3** shows the weak ν(CS) vibration at 785 cm<sup>−1</sup>. Besides this, an absorption peak at 2095 cm<sup>−1</sup> was observed for ν(CN) the stretching frequency of the thiocyanate group implying a different binding mode in accord with the X-ray analyses in that **3** exhibits a two-dimensional network featuring [Cu<sub>4</sub>Cd<sub>4</sub>(μ–SCN–S,N)<sub>8</sub>] and [Cu<sub>2</sub>Cd<sub>2</sub>(μ–SCN–S,N)<sub>4</sub>] subunits [7]. On the other hand, a non-coordinating thiocyanate group is present in complex **3** identified due to its very strong ν(CN) vibration at 2050 cm<sup>−1</sup> in the IR spectrum in Nujol mull. The presence of the solvate molecules in the complexes **1** and **2** can be observed by strong peaks at 1020 and 950 cm<sup>−1</sup> (for dmsO, **1**) and 1640 cm<sup>−1</sup> (for dmf, **2**).

The solid-state diffuse reflectance spectra of **1**–**3** show a similar pattern and exhibit absorptions

in the visible region centered between 18000 and 19500 cm<sup>−1</sup>, corresponding to d-d transitions in a distorted octahedral environment around copper(II) atoms [8], which is in agreement with the crystal structures. Besides the d-d bands, the spectra display ligand-to-metal charge transfer transitions at 28500 cm<sup>−1</sup> (for **1** and **2**) and at 32000 cm<sup>−1</sup> for **3**.

#### Structures of [Cu(en)<sub>2</sub>CdBr<sub>4</sub>]·dmsO (**1**), [Cu(en)<sub>2</sub>CdI<sub>4</sub>]·dmf (**2**)

The overall structural configurations for **1** and **2** are similar. Both complexes possess 1D chain structures formed by the tetrahedral CdX<sub>4</sub><sup>2−</sup> anions which behave as single-atom bridging ligands for square planar Cu(en)<sub>2</sub><sup>2+</sup> cations in *trans*-positions with Br or I atoms. There are only relatively small changes in bond lengths and angles (Table 2). The packing diagram and the numbering scheme of **1** are shown in Fig. 1 and the fragment of the crystal structure of **2** with its labeling scheme is shown in Fig. 2. The environment around the copper(II) atom in the Cu(en)<sub>2</sub><sup>2+</sup> part can be best described as a distorted octahedron with four nitrogen atoms of ethylenediamine molecules forming the basal plane, and with bromine (**1**) or iodine (**2**)

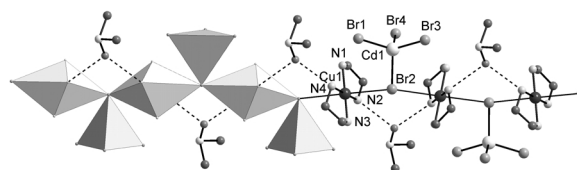


Fig. 1. The packing diagram with its numbering scheme of [Cu(en)<sub>2</sub>CdBr<sub>4</sub>]·dmsO (**1**). Hydrogen atoms are omitted for clarity.

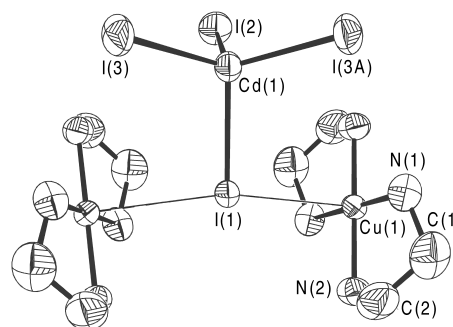


Fig. 2. Fragment of the crystal structure of the complex **2** with its labeling scheme. Hydrogen atoms are omitted for clarity.

atoms occupying the apical positions. Bond lengths in the en ligands are in accordance with those found for similar copper(II) complexes [4, 9, 10]. The apical Cu–X distances of 3.234(3) and 3.252(3) Å (**1**) and 3.300(1) Å (**2**) are quite long but close to those found in the literature [11]. The Cd(II) coordination environment closely approximates tetrahedral symmetry, the X–Cd–X bond angles being 107.1(1)–116.6(1)° in **1** and 100.78(5)–120.42(5)° in **2**. The non-equivalence of the Cd–X bond lengths suggest that the complex anions are *semi*-coordinated to the copper(II) atoms. The structures are supported by the dimethylsulfoxide (**1**) or dimethylformamide (**2**) molecules accommodated in the interchain space through hydrogen bonding to the amino-groups of the en ligands. The lengths of the en-solvate hydrogen bonds show the strongest connection for the dmsso molecule [ $d(\text{N} \cdots \text{O}_{\text{dmsso}})$  are 3.01(2) and 2.93(2) Å (**1**),  $d(\text{N} \cdots \text{O}_{\text{dmf}})$  are 2.98(1) Å (**2**)]. The chains of  $\text{Cu}^{\text{II}}\text{Cd}^{\text{II}}$  atoms have a zigzag shape with the angle CuCdCu dependent on the nature of the solvate molecule: 88.55(3)° (**1**), 81.73(2)° (**2**).

#### Structure of $[\{\text{Cu}(\text{en})_2\}_3\text{Cd}(\text{NCS})_6](\text{NCS})_2$ (**3**)

Fig. 3 shows the ORTEP drawing of the molecular structure of **3** together with the atom numbering scheme, while Fig. 4 and Fig. 5 show the 2D network character of the complex. Selected bond distances and bond angles are listed in Table 2.

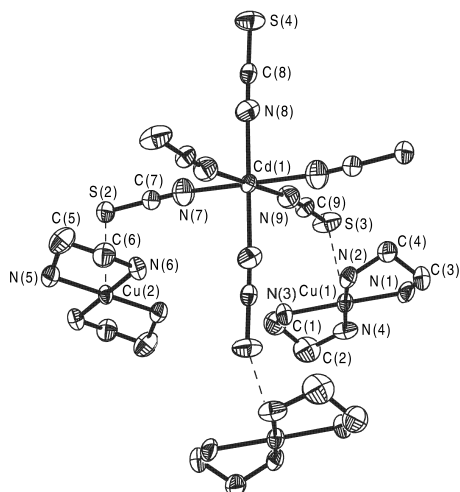


Fig. 3. ORTEP drawing of the dication  $[\{\text{Cu}(\text{en})_2\}_3\text{Cd}(\text{NCS})_6]^{2+}$  of **3** with 50% probability thermal ellipsoids, showing the atom numbering scheme (H atoms are omitted for clarity).

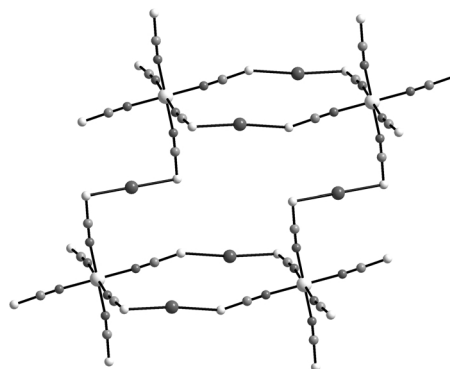


Fig. 4. A view of complex **3** showing the 32-membered rings  $[\text{Cu}_4\text{Cd}_4(\mu - \text{SCN} - \text{S}, \text{N})_8]$  and 16-membered rings  $[\text{Cu}_2\text{Cd}_2(\mu - \text{SCN} - \text{S}, \text{N})_4]$ .

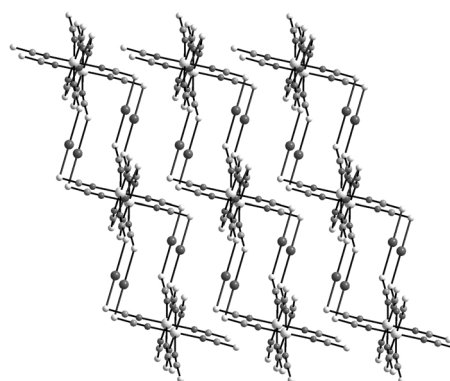


Fig. 5. Fragment of the 2D layer structure of complex **3** projected onto the  $xz$  plane.

The complex consists of three  $\text{Cu}(\text{en})_2^{2+}$  units and a  $\text{Cd}(\text{NCS})_6^{4-}$  fragment. Two non-coordinated  $\text{NCS}^-$  anions occupy cavities in the crystal lattice. The  $\mu - \text{NCS}$  ligands bridge adjacent Cu(II) and Cd(II) atoms to form a 2D array. The geometry around the cadmium ion is octahedral. The Cd–N distances vary between 2.306(8) and 2.348(7) Å and are longer than the typical values for octahedral coordination of cadmium thiocyanate complexes [12]. The N–Cd–N bond angles lie in the range 85.6(2)–94.4(2)°. The thiocyanate ligands are almost linear with a mean value of the N–C–S angles of 178.0°. The S–C distances in the range of 1.607(6)–1.637(7) Å and the C–N distances of 1.128(9)–1.49(1) Å are in accordance with the values observed in other thiocyanato-metal complexes [4, 13]. The coordination environment of the Cu(II) atom consists of two bidentate ethylenediamine ligands and two SCN bridging ligands coordi-

nated *via* their sulfur atoms. The copper(II) atoms have distorted octahedral coordination with  $N_4S_2$  donor sets. The Cu(1) centers have asymmetric (4+1+1) surroundings with the axial positions occupied by the S(3) and S(4) atoms [Cu(1)–S(3)=3.007(3) and Cu(1)–S(4)=3.124(3) Å] while Cu(2) has symmetric (4+2) surroundings [Cu(2)–S=3.032(2) Å]. The Cu–S bond distances are shorter than the sum of the van der Waals radii of Cu and S atoms (3.4 Å) [14] and similar to the values found in other complexes in which the sulfur atoms adopt an axial position in a distorted octahedron around copper(II) [15]. The four Cu–N bonds in the plane vary between 1.995(6) and 2.015(6) Å. The Cu(2)N<sub>4</sub> fragment is largely planar and its geometrical parameters are normal [16], in contrast to Cu(1)N<sub>4</sub> where the N(2) and N(4) atoms deviate strongly from the plane (0.144 and 0.019 Å, respectively). The rigid rod like nature of the thiocyanate ligand results in the formation of a 32-membered ring [Cu<sub>4</sub>Cd<sub>4</sub>(μ–SCN–S,N)<sub>8</sub>] in which a 16-membered [Cu<sub>2</sub>Cd<sub>2</sub>(μ–SCN–S,N)<sub>4</sub>] ring forms a section (Fig. 4). The intralayer Cd···Cu separations through a thiocyanate group are in the range 5.633(2)–7.878(9) Å.

The molecular shape of the cationic unit may influence the final structure. The Cu(en)<sub>2</sub><sup>2+</sup> fragment helps to template the formation of the extended structure of **3**, as reported for [Cu(en)<sub>2</sub>Au(CN)<sub>2</sub>][Au(CN)<sub>2</sub>] [9] and {[Cu(en)<sub>2</sub>][KCr(CN)<sub>6</sub>]} [17].

The title compounds represent examples of Cd(NCS)<sub>6</sub><sup>4–</sup> units which are quite rare for the cadmium ion. The ambidentate nature and the highly versatile bridging modes of the NCS<sup>–</sup> ligand allow the formation of a wide variety of polymeric metal-thiocyanate structures. We found only one instance

where thiocyanate groups are linked with a cadmium atom exceptionally *via* N atoms [18]. In **3** each cadmium atom is bonded exclusively to six hard N atoms of NCS<sup>–</sup> ions. In other words the Cd(II) ions are “harder” than the Cu(II) atoms, which are coordinated by the “soft” end of each thiocyanate ion (the S-atom). This rather unique environment of cadmium suggests unusual thermodynamic stability of the heterometallic polymer.

## Conclusion

Copper metal powder, cadmium oxide, ethylenediamine and an ammonium salt were employed successfully to synthesize heterometallic complexes, in air. The structures of the products **1–3** depend on the nature of the X<sup>–</sup> anion. In contrast to the analogues Cu/Zn compounds with a strongly restricted variation of their geometries, the Cu/Cd system is more versatile. [4]. Further work in our laboratories focuses on the use of different anions in the synthesis of new polymeric complexes apart from systematically investigating the role of dissimilar counter-ions in the formation of the architecture of extended networks.

## Supplementary material

Crystallographic data for compounds **1–3** have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), and are available on request quoting the deposition numbers CCDC 208557–208559.

## Acknowledgements

We thank the “Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich” (Project 15874-N03), for financial support.

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