

Direct synthesis as a new approach to heteropolynuclear complexes

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The idea of direct synthesis of coordination compounds – use of elemental metals or their oxides as starting materials – has been developed into “Salt route”, “Ammonium salt route” and “Direct template synthesis”, methods to synthesize heteropolynuclear complexes. The advantages of this approach in obtaining heterobi-, heterotrimetallic and mixed-anion heteropolynuclear coordination compounds are shown taking complexes of transition metals (Cu, Ni, Co, Mn, Zn, Cd) with aminoalcohols and ethylenediamine ligand as an example. The results of the X-ray crystal structure analysis and magnetic properties of the most interesting complexes are presented.

Key words: elemental metals; metal oxides; heteropolynuclear complexes; direct synthesis, crystal structure

1. Introduction

The design and synthesis of novel solid-state architectures using transition metal cations and multifunctional ligands enforcing metal bridging is a prolific domain in the field of coordination and materials chemistry [1]. The number of heteropolynuclear aggregates has increased enormously in recent years [2–4]. Interest in such nanoscale structures is due to a variety of potentially important applications from the areas of single molecule magnetism [5–7], photophysics [8], molecular electronics [9]. Furthermore, structural analysis of nanometer-sized heteropolynuclear molecules can give important insight into the early stages of nucleation [10], which is of relevance to all scientists working in areas such as nanoparticulates.

The distinct philosophies of “designed synthesis” and “self assembly” offer two main approaches to achieving the objective of creating new polynuclear materials with which to extend the range of present working theories. Synthetic difficulties in obtaining elaborate ligands and molecular synthons that can be used as ligands are

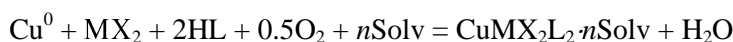
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a critical factor in restricting further studies because of the often tedious, costly and multi-step procedures.

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 a non-aqueous solution [11]. In this paper, an attempt is undertaken to show prospects of direct synthesis in preparations of heteropolynuclear complexes.

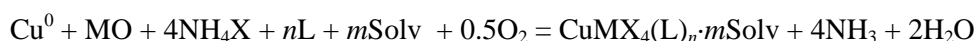
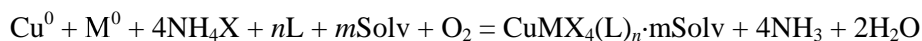
2. Heterobimetallic complexes

Developing the direct synthesis methodology we can offer two main routes for the preparation of heterobimetallic complexes. The first one, the so called "Salt route" method has been developed for protonic ligands. It can be illustrated by the reaction scheme to obtain heterobimetallic Cu-containing complexes with aminoalcohols (HL) as ligands:



where $M = \text{Ni, Co, Zn, Cd, Pb}$; $X = \text{Cl, Br, I, SCN, OAc}$; $\text{Solv} = \text{dmf, dmsO, CH}_3\text{OH, CH}_3\text{CN}$.

For the case of aprotic ligands the "Ammonium salt route" method can be used:



where $\text{M}^0 = \text{Co, Ni, Zn, Cd}$; $\text{MO} = \text{ZnO, CdO}$.

At the same time protonic ligands can be successfully used to prepare complexes by "Ammonium salt route" as well:



Some of heterobimetallic complexes obtained by the above mentioned routes [12–19] are shown in Table 1. The complexes with aminoalcohol ligands as a rule are built of polynuclear assemblies with the number of metal atoms that depends on the pair of metals chosen, the nature of aminoalcohol and anion.

Three heterotrinnuclear complexes $[\text{Cu}_2\text{Zn}(\text{NH}_3)\text{Cl}_3(\text{L}^2)_3]$ (**1**) $[\text{Cu}_2\text{Zn}(\text{NH}_3)\text{Br}_3(\text{L}^2)_3]$ (**2**) and $[\text{Cu}_2\text{Zn}(\text{NCS})_3(\text{L}^2)_3] \cdot \text{CH}_3\text{CN}$ (**3**) have been prepared using zerovalent copper, zinc oxide, an ammonium salt and 2-dimethylaminoethanol in air [17]. The overall structural configuration of **1** and **2** are similar. The trinuclear skeletons of **1** (Fig. 1) and **2** consist of a portion of a distorted cube in which alternate corners are non-metal (three oxygens and one chlorine) and metal atoms, and one corner metal site is vacant. The coordination geometry around the terminal, crystallographically independent copper atoms is distorted square pyramidal, $\text{Cu}(1)\text{N}_2\text{O}_2\text{X}$ and $\text{Cu}(3)\text{NO}_2\text{X}_2$, $X = \text{Cl}$ (**1**), Br (**2**).

Table 1. Some heterobinuclear complexes obtained by direct synthesis [12–24]¹

Initial system	Complex
Salt route	
$\text{Cu}^0\text{--PbX}_2\text{--HL}^1\text{--Solv}$	$\text{CuPbX}_2(\text{L}^1)_2 \cdot n\text{Solv}$ $\text{X} = \text{Cl, Br, I}$ $\text{Solv} = \text{dmsO, HL}^1; n = 0; 1$
$\text{Cu}^0\text{--MX}_2\text{--HL}^2\text{--Solv}$	$\text{Cu}_2\text{MX}_3(\text{L}^2)_3 \cdot \text{Solv}; \text{M} = \text{Co, Pb};$ $\text{X} = \text{Cl, I, NCS}; \text{Solv} = \text{CH}_3\text{CN, dmF, dmsO}$
$\text{Cu}^0\text{--CoX}_2\text{--H}_2\text{L}^2\text{--CH}_3\text{CN}$	$[\text{Cu}_2\text{Co}(\mu_3\text{-OH})\text{Br}_2(\text{L}^2)_3]_2 \cdot 2\text{CH}_3\text{CN}$ $[\text{Cu}_2\text{Co}(\mu_3\text{-OH})\text{I}_2(\text{L}^2)_3]_2 \cdot 4\text{CH}_3\text{CN}$
$\text{Cu}^0\text{--Co(OAc)}_2\text{--H}_3\text{L}^4\text{--Solv}$	$[\text{Cu}_2\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{OAc})_4(\text{H}_2\text{L}^4)_2(\text{L}^4)_2] \cdot 2\text{HOAc}$
Ammonium salt route	
$\text{Cu}^0\text{--ZnO--NH}_4\text{X--HL}^2\text{--Solv}$	$\text{Cu}_2\text{Zn}(\text{NH}_3)_n\text{X}_3(\text{L}^2)_3 \cdot m\text{CH}_3\text{CN}$ $\text{X} = \text{Cl, Br, I, NCS}; n = 0; 3, m = 0; 1$
$\text{Cu}^0\text{--ZnO--NH}_4\text{Br--HL}^3\text{--CH}_3\text{OH}$	$[\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HL}^3)_4]\text{Br}_2 \cdot \text{CH}_3\text{OH}$
$\text{Cu}^0\text{--ZnO--NH}_4\text{X--en--Solv}$ $\text{Solv} = \text{CH}_3\text{OH, CH}_3\text{CN, dmF, dmsO}$	$[\text{Cu}(\text{en})_2\text{ZnX}_4] \cdot n\text{Solv} \text{ X} = \text{Cl, Br, I, NCS, OAc}$ $\text{Solv} = \text{H}_2\text{O, CH}_3\text{CN, dmF, dmsO}; n = 0; 0.5; 1$
$\text{Cu}^0\text{--CdO--NH}_4\text{X--en--Solv}$ $\text{Solv} = \text{CH}_3\text{OH, CH}_3\text{CN, dmF, dmsO}$	$[\text{Cu}(\text{en})_2\text{CdX}_4] \cdot n\text{Solv} \text{ X} = \text{Cl, Br, I,}$ $\text{Solv} = \text{dmF, dmsO}; n = 0; 1$
$\text{Cu}^0\text{--CdO--NH}_4\text{OAc--en--Solv}$ $\text{Solv} = \text{CH}_3\text{OH, CH}_3\text{CN, dmF, dmsO}$	$[\text{Cu}(\text{en})_2][\text{Cd}_2(\text{OAc})_6]$
$\text{Cu}^0\text{--CdO--NH}_4\text{NCS--en--CH}_3\text{OH}$	$[\{\text{Cu}(\text{en})_2\}_3\text{Cd}(\text{NCS})_6](\text{NCS})_2$
Salt route + Ammonium salt route	
$\text{Cu}^0\text{--Cd(OAc)}_2\text{--NH}_4\text{X--en--Solv}$ $\text{Solv} = \text{CH}_3\text{OH, dmF, dmsO}$	$[\text{Cu}(\text{en})_2\text{Cd}(\text{OAc})_2\text{X}_2]$ $\text{X} = \text{Cl, Br}$
$\text{Cu}^0\text{--Cd(OAc)}_2\text{--NH}_4\text{I--en--Solv}$ $\text{Solv} = \text{dmF, dmsO}$	$[\text{Cu}(\text{en})_2\text{CdI}(\text{OAc})_3]$
$\text{Cu}^0\text{--Cd(OAc)}_2\text{--NH}_4\text{NCS--en--Solv}$ $\text{Solv} = \text{CH}_3\text{OH, CH}_3\text{CN, dmF}$	$[\text{Cu}_2(\text{en})_4\text{Cd}_2(\text{OAc})_2(\text{NCS})_6]$
$\text{Cu}^0\text{--Cd(dca)}_2\text{--NH}_4\text{NCS--en--CH}_3\text{OH}$	$[\text{Cu}(\text{en})_2\text{Cd(dca)}_2(\text{NCS})_2]$
$\text{ZnO--NiX}_2\text{--NH}_4\text{X--en--Solv}$ $\text{Solv} = \text{CH}_3\text{OH, CH}_3\text{CN, dmF, dmsO}$	$[\text{Ni}(\text{en})_3][\text{ZnX}_4] \cdot n\text{Solv} \text{ X} = \text{Cl, Br, NCS}$ $\text{Solv} = \text{CH}_3\text{CN, dmsO}; n = 0; 1; 2$
$\text{CdO--NiX}_2\text{--NH}_4\text{X--en--Solv}$ $\text{Solv} = \text{CH}_3\text{OH, CH}_3\text{CN, dmF, dmsO}$	$[\text{Ni}(\text{en})_3][\text{CdX}_4] \cdot n\text{Solv} \text{ X} = \text{Cl, Br}$ $\text{Solv} = \text{dmsO}; n = 0; 3$
$\text{CdO--NiBr}_2\text{--NH}_4\text{Br--en--dmF}$	$[\text{Ni}(\text{en})_2(\text{dmF})_2][\text{CdBr}_4]$
$\text{CdO--Ni(NCS)}_2\text{--NH}_4\text{NCS--en--CH}_3\text{CN}$	$[\text{Ni}_2(\text{en})_4\text{Cd}(\text{NCS})_6] \cdot \text{CH}_3\text{CN}$

¹HL¹ – 2-aminoethanol, HL² – 2-dimethylaminoethanol, H₂L³ – diethanolamine, H₃L⁴ – triethanolamine, dca – N(CN)₂[–].

Complex $[\text{Cu}_2\text{Zn}(\text{NCS})_3(\text{L}^2)_3] \cdot \text{CH}_3\text{CN}$ has a symmetrical trinuclear core similar to that of **1** and **2** (Fig. 2). The copper atom adopts a square-pyramidal coordination sphere, with a chromophore $\{\text{CuN}_2\text{O}_2\text{S}\}$ in which the axial atom belongs to a thiocyanate group of the neighbouring molecule. Intermolecular association in the structure of **3** occurs through the Cu–S interactions between the S(2) atom of the SCN-group

coordinated to Zn(1) and two copper atoms of the adjacent complex molecule. As a consequence, a polymeric chain assembly is evident along the *c*-axis of the crystal (Fig. 2).

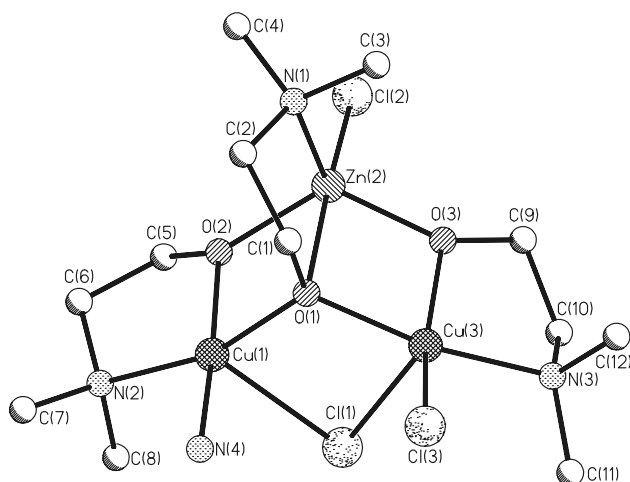


Fig. 1. Molecular structure of $[\text{Cu}_2\text{Zn}(\text{NH}_3)\text{Cl}_3(\text{L}^2)_3]$, showing the atom numbering scheme (H atoms omitted for clarity) [17]

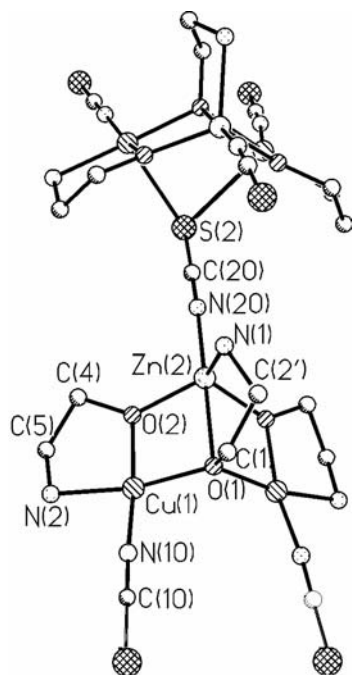


Fig. 2. Molecular structure of $[\text{Cu}_2\text{Zn}(\text{NCS})_3(\text{L}^2)_3] \cdot \text{CH}_3\text{CN}$ with the atom numbering scheme, showing the intermolecular Cu-S_{NCS} interactions in a polymeric chain (H atoms omitted for clarity) [17]

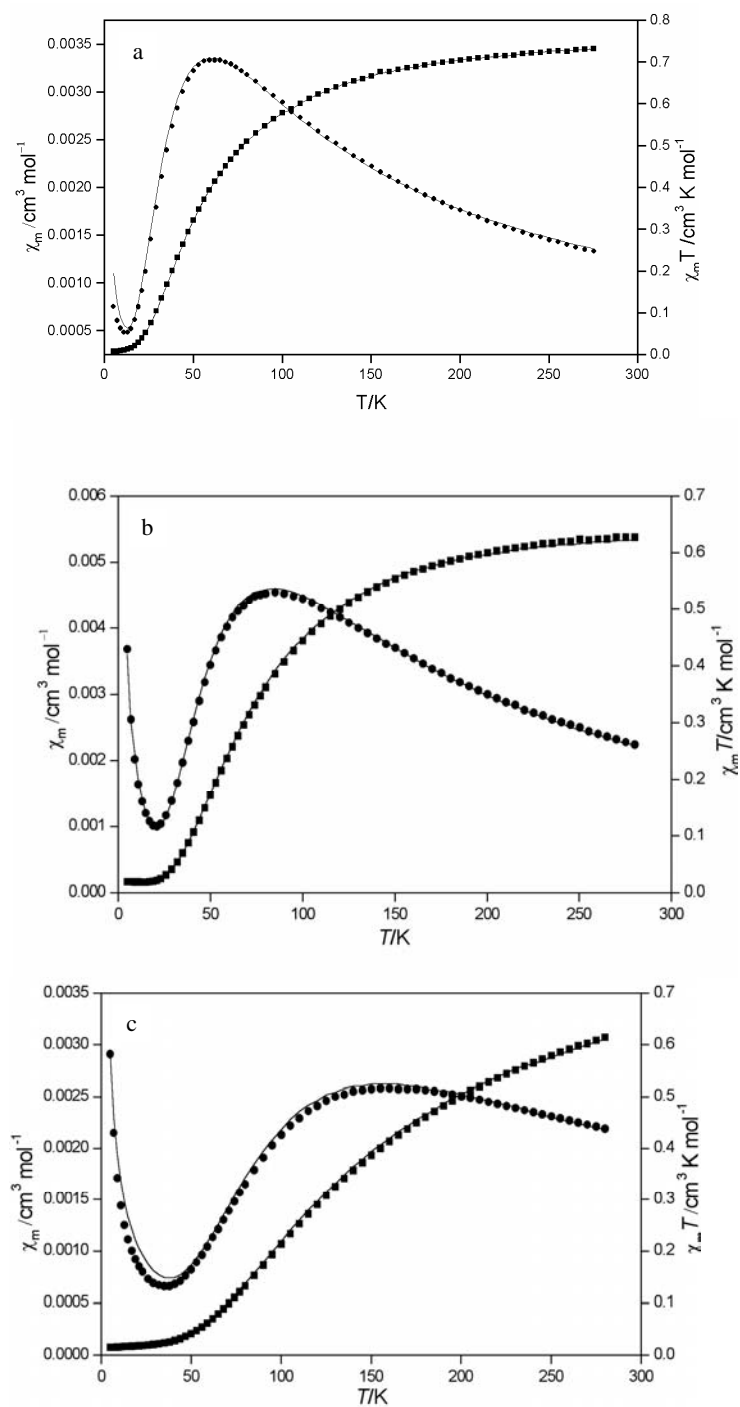


Fig. 3. Plots of χ_m (dots) and $\chi_m T$ (squares) vs. T for complexes: $[\text{Cu}_2\text{Zn}(\text{NH}_3)\text{Cl}_3(\text{L}^2)_3]$ (a), $[\text{Cu}_2\text{Zn}(\text{NH}_3)\text{Br}_3(\text{L}^2)_3]$ (b) and $[\text{Cu}_2\text{Zn}(\text{NCS})_3(\text{L}^2)_3] \cdot \text{CH}_3\text{CN}$ (c) [17]

The magnetic susceptibility per half of the molecule of **4** shown in Fig. 5 increases with decreasing temperature to reach a maximum at ca. 30 K and then decreases with further temperature lowering. This behaviour is typical of an antiferromagnetic spin exchange operating in the Cu_2Zn_2 units of ($J = 35.0 \text{ cm}^{-1}$) [18].

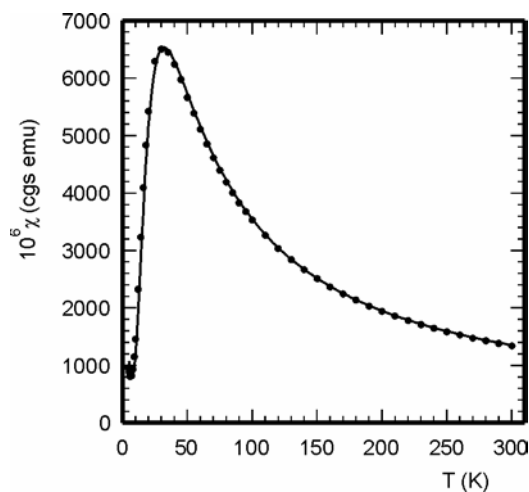


Fig. 5. Magnetic susceptibility per 1/2 mole vs. T for complex $[\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HL}^3)_4]\text{Br}_2 \cdot \text{CH}_3\text{OH}$ [18]

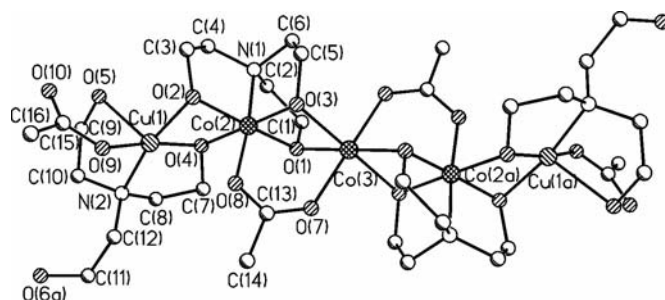


Fig. 6. Structure of pentanuclear unit in $[\text{Cu}_2\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{OAc})_4(\text{H}_2\text{L}^4)_2(\text{L}^4)_2] \cdot 2\text{HOAc}$ [16]

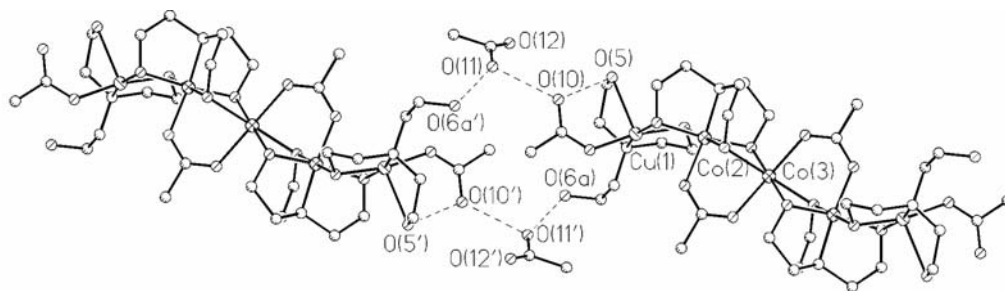


Fig. 7. View of $[\text{Cu}_2\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{OAc})_4(\text{H}_2\text{L}^4)_2(\text{L}^4)_2] \cdot 2\text{HOAc}$ showing the hydrogen-bonded network involving the non-coordinating acetic acid molecules [16]

Reaction of zerovalent copper with cobalt(II) acetate and triethanolamine in dmf solution in air yields the unique mixed-valence complex $[\text{Cu}_2\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{OAc})_4(\text{H}_2\text{L}^4)_2(\text{L}^4)_2]\cdot 2\text{HOAc}$ (**5**) [16]. The complex consists of the pentanuclear unit $[\text{Cu}_2\text{CoCo}_2(\text{OAc})_4(\text{H}_2\text{L}^4)_2(\text{L}^4)_2]$, which has an inversion centre (Fig. 6) and two molecules of acetic acid in the crystal lattice. The five metal ions are linked together by eight oxygen atoms of the four triethanolamine ligands and by two acetate groups with metal–metal separations being 2.823(2) and 2.964(1) Å for Cu(1)...Co(2) and Co(2)...Co(3), respectively. The divalent cobalt atom, Co(3), is located at the centre of inversion, and its coordination geometry can be best described as a slightly distorted octahedron. The geometry at the trivalent cobalt atoms, Co(2) and Co(2a), is distorted octahedral. The atom Cu(1) is five-coordinate with square-pyramidal geometry. Two non-coordinating acetic acid molecules are connected to the pentanuclear unit *via* hydrogen bonds. The intermolecular hydrogen bonding links the pentanuclear units together and results in the formation of an extended one-dimensional structure (Fig. 7).

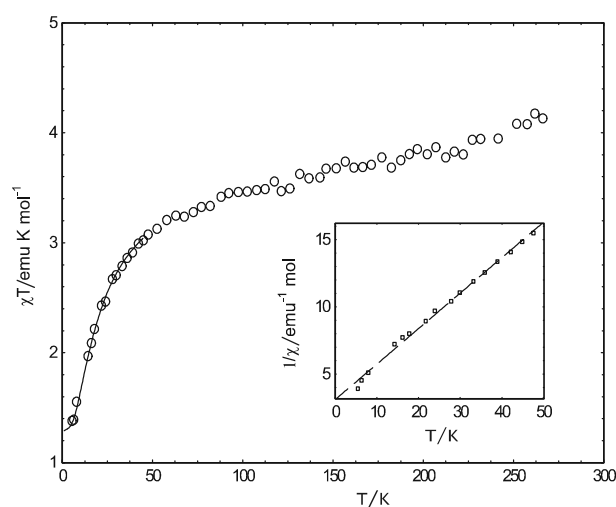


Fig. 8. $\chi_m T$ vs. T curve for $[\text{Cu}_2\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{OAc})_4(\text{H}_2\text{L}^4)_2(\text{L}^4)_2]\cdot 2\text{HOAc}$ [16]

At room temperature the value of $\chi_m T$ ($4.1 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) (Fig. 8) is in agreement with the presence of two uncorrelated $S = 1/2$ centres and one $S = 3/2$ centre with largely unquenched angular orbital momentum. Magnetic measurements showed a marked decrease of the $\chi_m T$ value at low temperature, indicative of antiferromagnetic interactions between magnetic centres. A fit was attempted assuming an effective $S = 1/2$ ground state for Co(II) and Ising-type anisotropy, considering only intramolecular interactions. The obtained value for $J_z = 36 \text{ cm}^{-1}$ must originate from the efficient role of the diamagnetic Co(III) in the transmitting the interaction between Cu(II) and Co(II) below 40 K [16].

The reaction of acetonitrile solutions of $\text{CoX}_2\cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{Br}, \text{I}$) and 2-dimethylaminoethanol with copper powder in the air leads to the formation hexanuclear com-

plexes $[\text{Cu}_2\text{Co}(\mu_3\text{-OH})\text{Br}_2(\text{L}^2)_3]_2 \cdot 2\text{CH}_3\text{CN}$ (**6**) and $[\text{Cu}_2\text{Co}(\mu_3\text{-OH})\text{I}_2(\text{L}^2)_3]_2 \cdot 4\text{CH}_3\text{CN}$ (**7**) [15]. In the structure of **6** and **7** (Fig. 9) two symmetry-related Cu_2Co units are linked by amino alkoxo bridges to form a hexanuclear molecule with intermetallic distances ranging from 3.102(2)–3.260(2) (Cu...Co) to 3.287(3)–3.931(2) Å (Cu...Cu). The triangular planes formed by two copper and one cobalt atoms are capped by a $\mu_3\text{-OH}$ group that adopts an asymmetric bonding mode with two shorter distances (mean 1.962(9) Å) to the copper atoms and longer one to the cobalt centre (mean 2.293(10) Å). The two copper centres have distinct chemical environments but both adopt a distorted square-pyramidal coordination. The two copper square pyramids are tilted toward each other as a result of the bridging function of the axial halide atom. Five-coordination of the cobalt atom is completed by three oxygen atoms, one nitrogen atom and the $\mu_3\text{-hydroxide}$ in an elongated trigonal bipyramidal geometry.

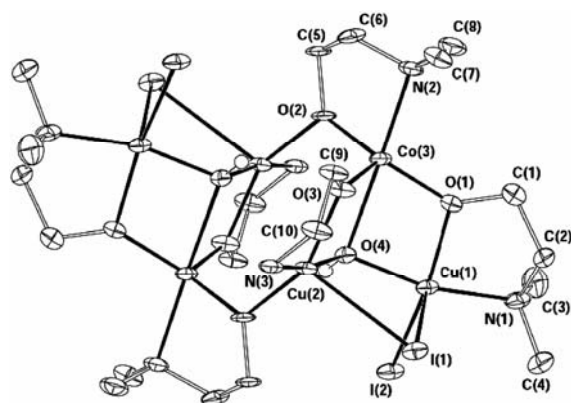


Fig. 9. ORTEP plot of $[\text{Cu}_2\text{Co}(\mu_3\text{-OH})\text{I}_2(\text{L}^2)_3]_2 \cdot 4\text{CH}_3\text{CN}$ with the atom numbering scheme [15]

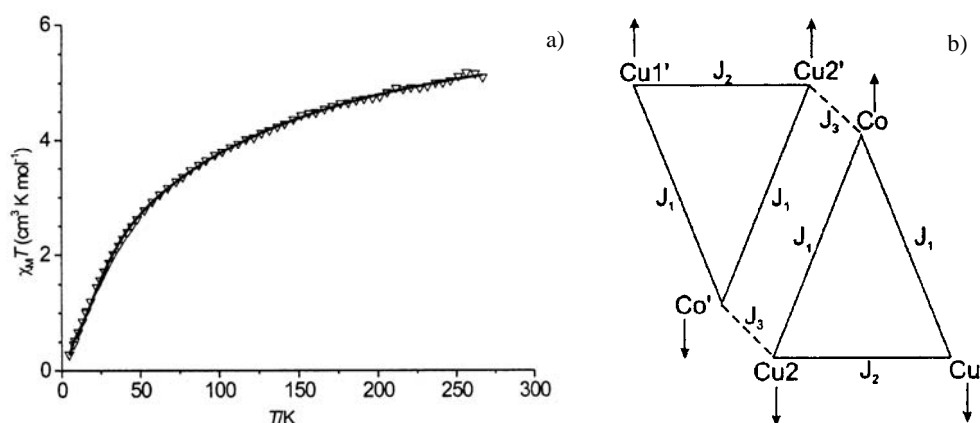


Fig. 10. $\chi_m T$ vs. T curve for $[\text{Cu}_2\text{Co}(\mu_3\text{-OH})\text{I}_2(\text{L}^2)_3]_2 \cdot 4\text{CH}_3\text{CN}$ (a) and exchange coupling pattern with the scheme of the spin topology (b) [15]

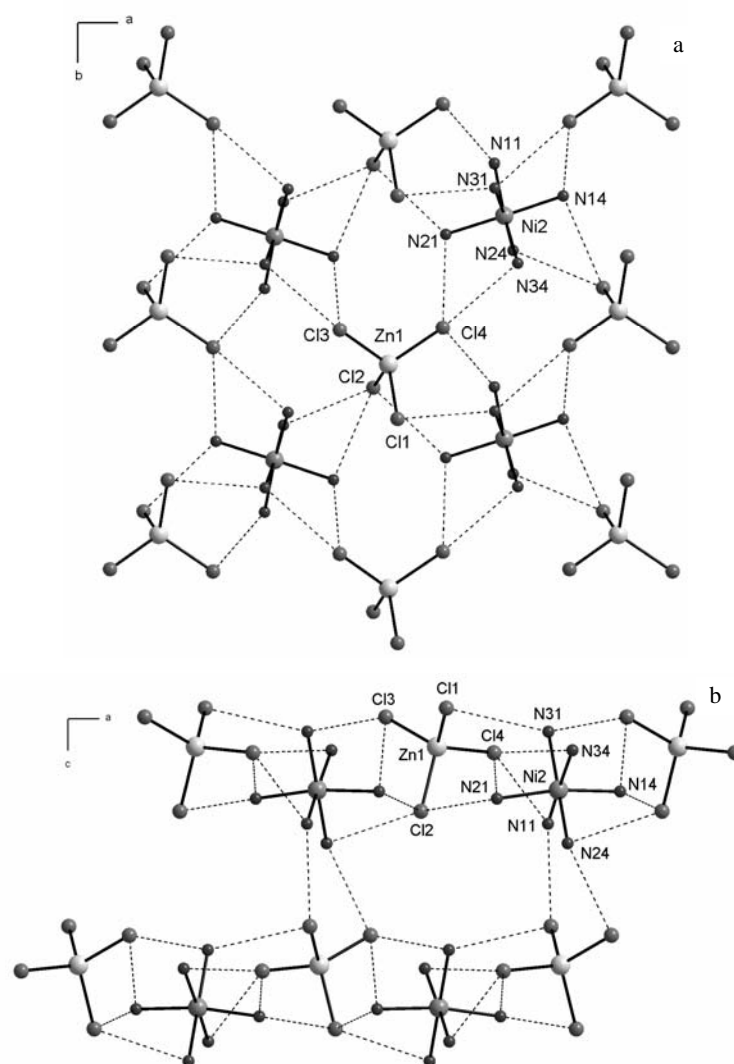


Fig. 11. View of a fragment of the 2D layer projected onto the *ab* plane (a) and a packing diagram of the sheets (b) of $[\text{Ni}(\text{en})_3][\text{ZnCl}_4]$ [19]

The magnetic susceptibility data for **7** have been quantitatively analysed in the 5–280 K temperature range (Fig. 10) on the assumption of isotropic coupling between the magnetic centres as the ground electronic state of the trigonal bipyramidal Co(II) centre is orbitally non-degenerate. Variable-temperature magnetic susceptibility study gave satisfactory fits to the observed susceptibility considering **7** as a combination of two trinuclear entities. An antiferromagnetic spin exchange operates in the Cu_2Co unit ($J_{\text{CuCu}} = 48.7(9)$; $J_{\text{CuCo}} = 86.2(1.3) \text{ cm}^{-1}$) while a weak ferromagnetic coupling is active between Cu and Co atoms from different trinuclear entities ($J_{\text{CuCo}'} = -8.0(4) \text{ cm}^{-1}$) [15].

A bridging mode is not typical of ethylenediamine. Therefore the replacement of aminoalcohol with en results in the dramatic change of the structure of heteropolynuclear complexes. The anions overtake bridging functions and a role of hydrogen bonds becomes more important. The increase of inter-metal distances prevents from exchange interactions.

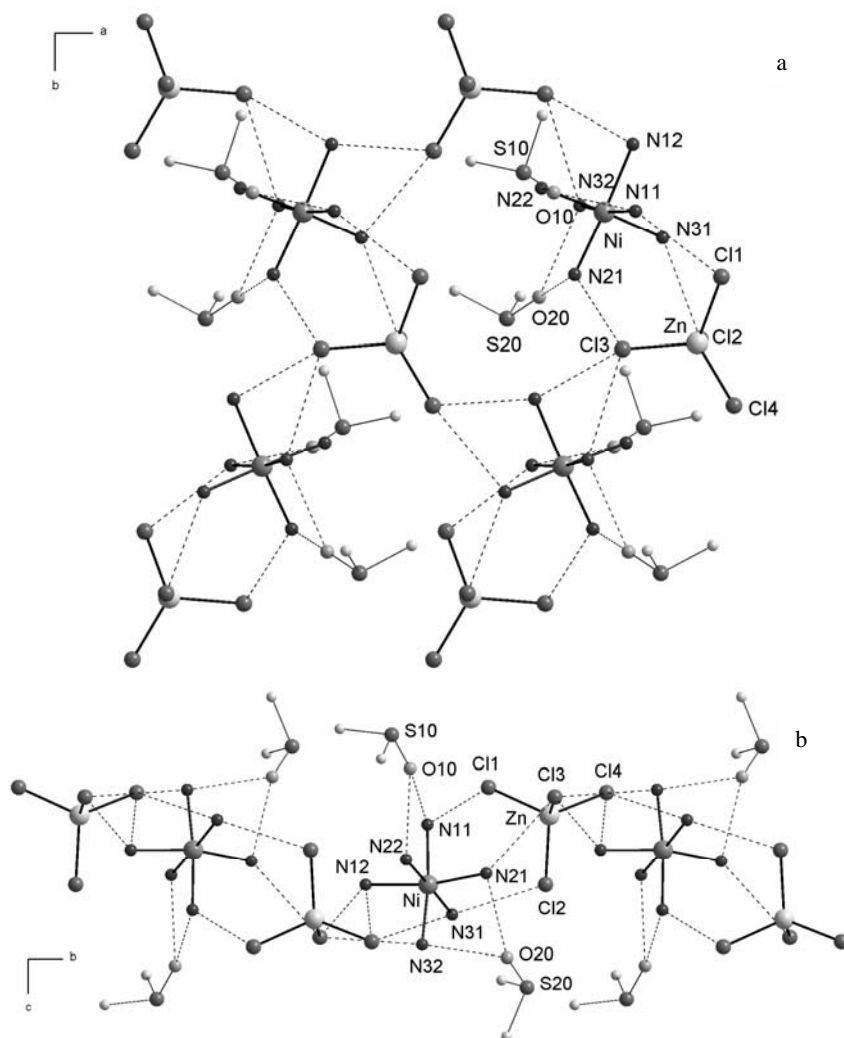


Fig. 12. H-bonding motifs generating infinite 2D sheets in $[\text{Ni}(\text{en})_3][\text{ZnCl}_4] \cdot 2\text{dmsO}$ (a) and a view of the complex projecting onto the cb plane (b) [19]

Heterobimetallic complexes $[\text{Ni}(\text{en})_3][\text{ZnCl}_4]$ (**8**), $[\text{Ni}(\text{en})_3][\text{ZnCl}_4] \cdot 2\text{dmsO}$ (**9**) and $[\text{Ni}(\text{en})_3][\text{Zn}(\text{NCS})_4] \cdot \text{CH}_3\text{CN}$ (**10**) have been synthesized in the open-air reaction of zinc oxide, nickel chloride (or nickel powder), NH_4X ($\text{X} = \text{Cl}, \text{NCS}$) and ethylenediamine in non-aqueous solvents [19]. Complex **8** consists of $[\text{Ni}(\text{en})_3]^{2+}$ and

$[\text{ZnCl}_4]^{2-}$ ions that form a three-dimensional network by means of H-bonds (Fig. 11). Between the anion and cation, a lot of intermolecular $\text{N-H}\cdots\text{Cl}$ interactions, which indicate weak extensive hydrogen bonding, are found and one $[\text{Ni}(\text{en})_3]^{2+}$ unit is hydrogen bonded to five different anions (four in the 2D layer and one between adjacent sheets).

Compound **9** made of the same building blocks ($[\text{Ni}(\text{en})_3]^{2+}$ cations and $[\text{ZnCl}_4]^{2-}$ anions) also contains two molecules of dimethylsulfoxide, the presence of which causes considerable changes in the crystal architecture (Fig. 12). The plentiful array of hydrogen bonds, that occur as in all described complexes, strengthen the structure, but in contrast to **8**, the $[\text{Ni}(\text{en})_3]^{2+}$ unit is hydrogen-bonded to only three different $[\text{ZnCl}_4]^{2-}$ anions instead of five different $[\text{ZnCl}_4]^{2-}$ anions (as in the case in **8**) being additionally H-bonded to two dmso molecules. All the chlorine atoms are linked by means of H-bonds with amino groups of the ethylenediamine of the cations, and one of them is 3-coordinated by H(N) atoms, one 2-coordinated and two unbranched. These listed hydrogen bonds are stabilized the two-dimensional sheets of **9**, which are slightly undulating in comparison with **8**, but further interlayer H-bonds are now not possible due to the presence of the dmso solvent molecules [19].

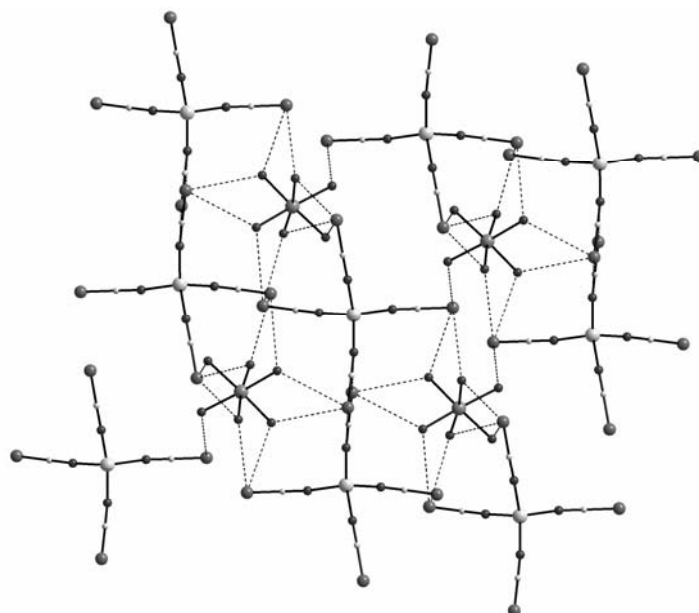


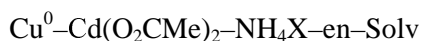
Fig. 13. Packing diagram of $[\text{Ni}(\text{en})_3][\text{Zn}(\text{NCS})_4]\cdot\text{CH}_3\text{CN}$ projected onto the ac plane showing a 3D network generated by hydrogen bonds [19]

The compound $[\text{Ni}(\text{en})_3][\text{Zn}(\text{NCS})_4]\cdot\text{CH}_3\text{CN}$ consists of the $[\text{Ni}(\text{en})_3]^{2+}$ cations and $[\text{Zn}(\text{NCS})_4]^{2-}$ anions, the presence of which facilitate formation of a three-dimensional architecture based on numerous $\text{N-H}\cdots\text{S}$ hydrogen bonds (Fig. 13). The geometrical parameters of the $[\text{Ni}(\text{en})_3]^{2+}$ unit are similar to those found in **8** and **9**. The crystal

structure of **10** is reinforced by several hydrogen bonds and the $[\text{Ni}(\text{en})_3]^{2+}$ unit is H-bonded to five different $[\text{Zn}(\text{NCS})_4]^{2-}$ anions and a molecule of CH_3CN . All four S atoms joined with NH_2 groups of $[\text{Ni}(\text{en})_3]^{2+}$ cations using hydrogen bonds, and two of them are 3-coordinated by H(N) atoms and two – 2-coordinated [19]. Such an essential influence of the nature of the anion on the nuclearity and coordination topology can be used for the regulative change of the structure of the heteropolynuclear complex by the synthesis of compounds with a necessary combination of anions. The possibility of the synthesis of heteropolynuclear complexes with a certain set of anions of different nature can be achieved with the combination of “Salt” and “Ammonium salt” methods of direct synthesis:



Moreover, such a combination makes it possible to prepare mixed-metal mixed-anion complexes in “one pot”. Thus, to prepare mixed-anion heterobimetallic coordination polymers $[\text{Cu}(\text{en})_2\text{Cd}(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})\text{Cl}(\text{O}_2\text{CMe})]_n$ (11), $[\text{Cu}(\text{en})_2\text{CdI}_{1.64}(\text{O}_2\text{CMe})_{2.36}]_n$ (12), $[\text{Cu}_2(\text{en})_4\text{Cd}_2(\text{NCS})_2(\text{NCS})_4(\text{O}_2\text{CMe})_2]_n$ (13) the following systems have been used [20]:



where X = Cl, Br, I, NCS; Solv = dmf, dmsO, CH_3OH , CH_3CN .

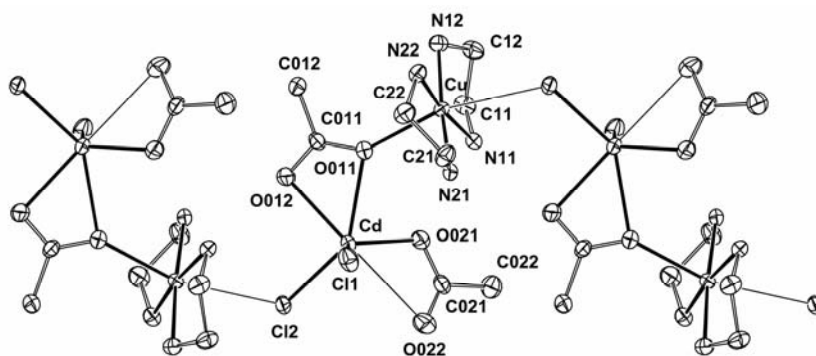


Fig. 14. The one-dimensional helical chain in the compound $[\text{Cu}(\text{en})_2\text{Cd}(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})\text{Cl}(\text{O}_2\text{CMe})]_n$ with the numbering scheme [20]

The structure of compound **11** consists of an infinite one-dimensional helical chain comprised of cationic $\text{Cu}(\text{en})_2^{2+}$ and mixed-ligand anionic $\text{Cd}(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})\text{Cl}(\text{O}_2\text{CMe})^{2-}$ building blocks, linking together through one bridging chlorine atom and an oxygen atom of the chelating (and also bridging) bidentate acetate ligand (Fig. 14). The Cd atom in **11** is six-coordinate; the coordination sphere consisting two acetate groups, one of which is weakly bidentate, the other one being bidentate [through O(011) and O(012)] and bridging unidentate [through O(011)]. Each of

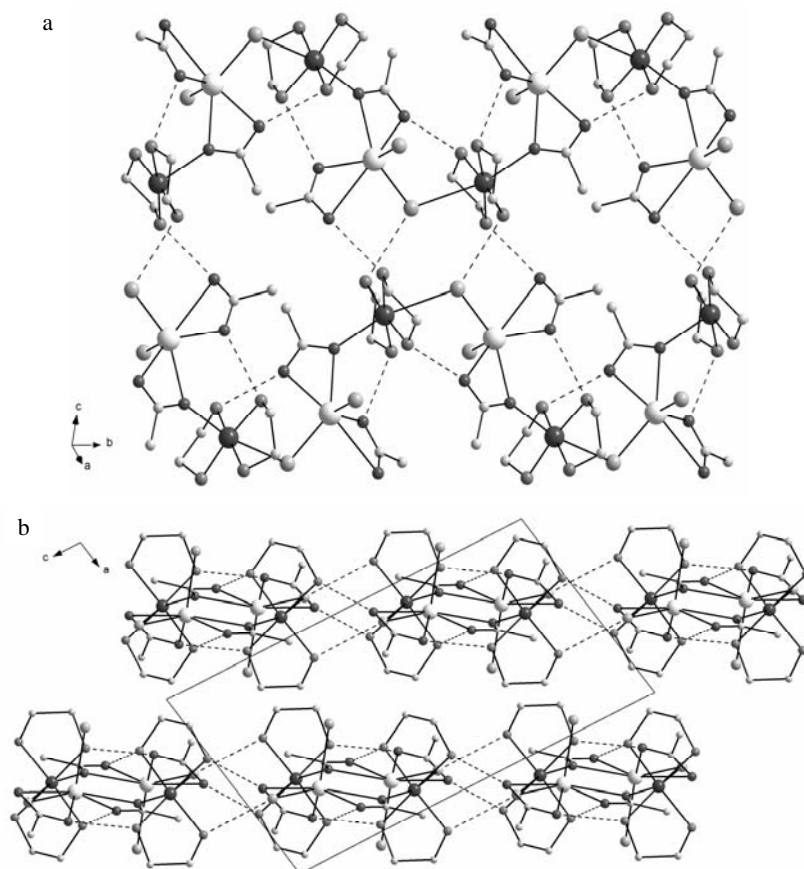


Fig. 15. Fragment of the 2D sheet (a) and a view of the layer arrangement (b) in the structure of $[\text{Cu}(\text{en})_2\text{Cd}(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})\text{Cl}(\text{O}_2\text{CMe})]_n$ [20]

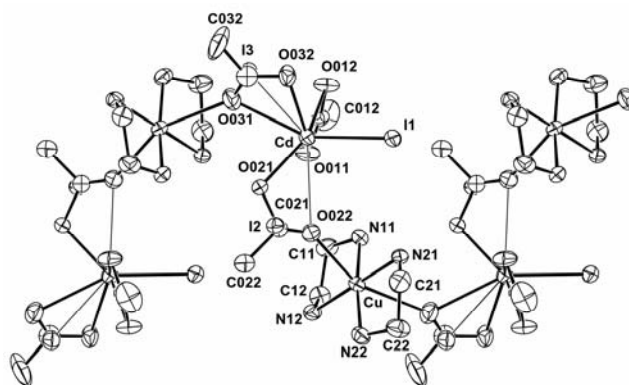


Fig. 16. Perspective view of a helical chain in complex $[\text{Cu}(\text{en})_2\text{CdI}_{1.64}(\text{O}_2\text{CMe})_{2.36}]_n$ together with the atom numbering [20]

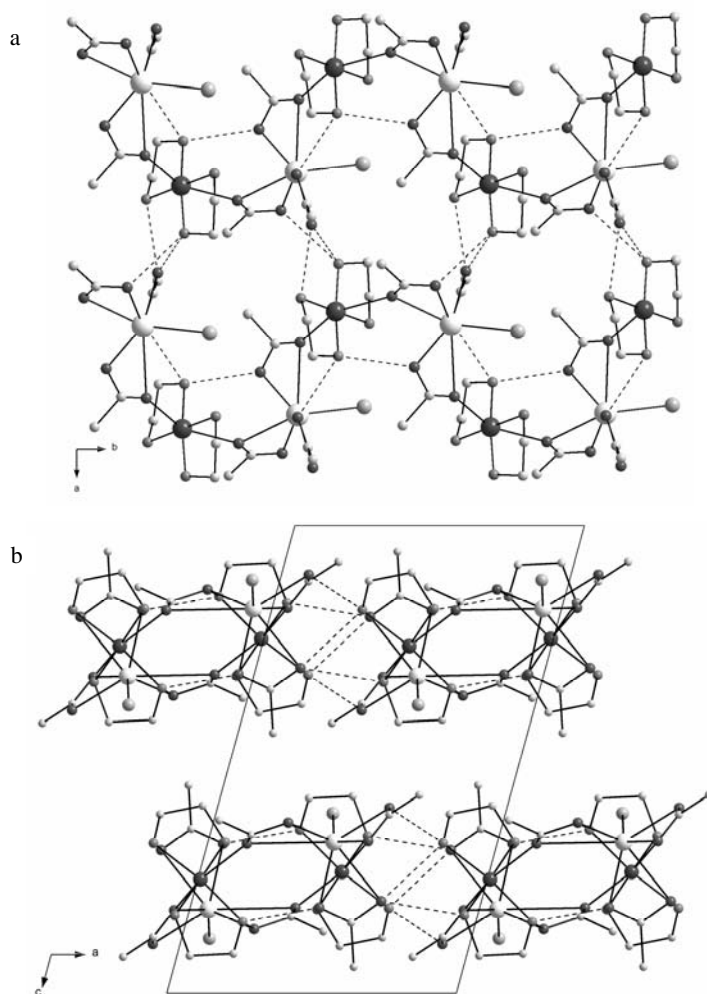


Fig. 17. View of a fragment of the 2D layer (a) and a packing diagram of the polymeric sheets (b) in complex $[\text{Cu}(\text{en})_2\text{CdI}_{1.64}(\text{O}_2\text{CMe})_{2.36}]_n$ [20]

the Cd(II) is further coordinated by one terminal and one bridging chlorine atom to form a CdO_4Cl_2 distorted octahedron. The chains of $\text{Cu}-\text{Cl}(2)-\text{Cd}-\text{O}(011)$ atoms reveal a helical shape. Two sets of H-bonds assemble the chains, related by the crystallographic planes into a two-dimensional structure (Fig. 15) [20]. The complex **12** is basically 1D helical chain structure formed by $\text{Cu}(\text{en})_2^{2+}$ units and $\text{Cd}(\mu-\text{O}_2\text{CMe})_2\text{I}(\text{O}_2\text{CMe})^{2-}$ building blocks, which are joined through oxygen atom from a weakly bidentate chelate acetate ligand and also through the oxygen atoms of the other acetate group which is bridging unidentate and bidentate (Fig. 16). However both bridging acetate sites are also partially occupied by iodide ions. Thus as well as bridging $\text{Cd}(\mu-\text{O}_2\text{CMe})_2\text{I}(\text{O}_2\text{CMe})^{2-}$ units, there is also a minor component of $\text{Cd}(\mu-\text{O}_2\text{CMe})(\mu-\text{I})\text{I}(\text{O}_2\text{CMe})^{2-}$. There may also be some $\text{Cu}(\text{en})_2\text{Cd}(\mu-\text{I})_2\text{I}(\text{O}_2\text{CMe})^{2-}$ corresponding the

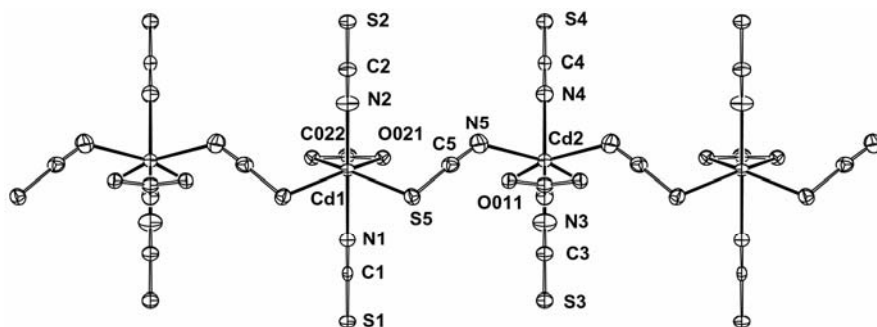


Fig. 18. View of the anionic chain motif of complex $[\text{Cu}_2(\text{en})_4\text{Cd}_2(\text{NCS})_2(\text{NCS})_4(\text{O}_2\text{CMe})_2]_n$ together with the atom numbering scheme [20]

replacement of both bridging acetates. In **12** only one nitrogen atom from NH_2 group of en takes part in the intrachain hydrogen bonding with oxygen atoms of the acetate ligands, in contrast with two N_{en} atoms that participated in H-bonding in **11**. Furthermore, only one type of H-bonding interactions, those involving a hydrogen atom of an NH_2 group of en and an oxygen atom of a bidentate acetate group, facilitates the formation of 2D sheets (Fig. 17) [20].

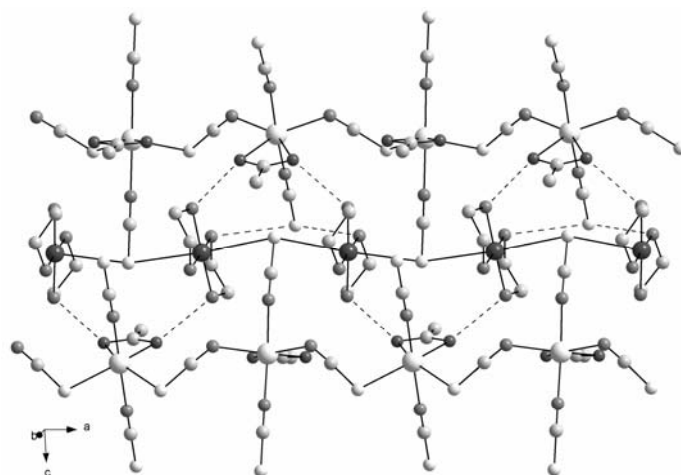


Fig. 19. Perspective view of a sheet in complex $[\text{Cu}_2(\text{en})_4\text{Cd}_2(\text{NCS})_2(\text{NCS})_4(\text{O}_2\text{CMe})_2]_n$ [20]

X-Ray analysis reveals a two-dimensional wave-like polymeric network for complex **13**, the crystal structure of which consists of 1D anionic chains of $\text{Cd}_2(\text{NCS})_6(\text{O}_2\text{CMe})_2^{4-}$ and $\text{Cu}(\text{en})_2^{2+}$ units. The view of the 1D anionic chain motif together with the atom numbering scheme is presented in Fig. 18, while Fig. 19 shows the perspective view of a 2D sheet. Both copper(II) and cadmium(II) atoms are joined through $-\text{Cu}-\text{SCN}-\text{Cd}-$ linkages. The polymeric anion contains two crystallographically independent cadmium atoms, Cd(1) and Cd(2), both of which are six-coordinate with

$\text{CdS}_2\text{N}_2\text{O}_2$ and CdN_4O_2 distorted octahedral geometries, respectively. Both Cd(II) atoms are coordinated by one chelating bidentate acetate group, one terminal thiocyanate ligand, one $\mu_{1,3}$ -NCS group, which connect the copper(II) and cadmium(II) atoms in the 2D layer, and another two $\mu_{1,3}$ -NCS groups which serve bridges between the metal centres. The polymeric mixed-anion $-\text{NCS}-\text{Cd}(\text{NCS})_2(\text{O}_2\text{CMe})-\text{SCN}-\text{Cd}(\text{NCS})_2(\text{O}_2\text{CMe})-\text{NCS}-$ chains are almost linear. The resulting 2D sheets consist of 18-membered $[\text{Cd}_3(\mu_{1,3}\text{-NCS})_4\text{Cu}_2\text{S}_{\text{NCS}}]$ rings folded in a wave-like manner (Fig. 19) [20].

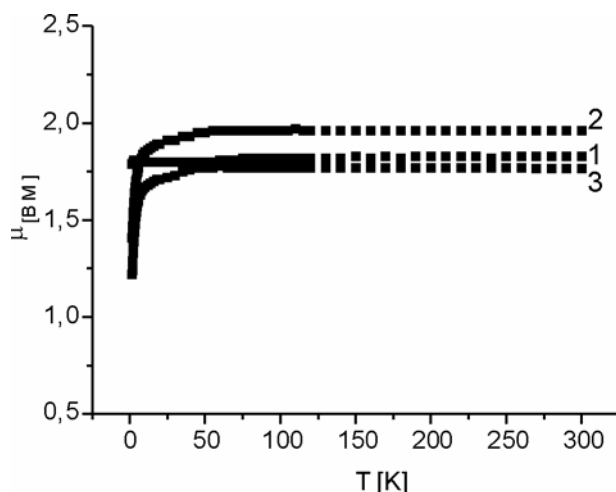


Fig. 20. Temperature dependences of the effective magnetic moment for $[\text{Cu}(\text{en})_2\text{Cd}(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})\text{Cl}(\text{O}_2\text{CMe})]_n$, (1) $[\text{Cu}(\text{en})_2\text{CdI}_{1.64}(\text{O}_2\text{CMe})_{2.36}]_n$ (2) and $[\text{Cu}_2(\text{en})_4\text{Cd}_2(\text{NCS})_2(\text{NCS})_4(\text{O}_2\text{CMe})_2]_n$ (3) [20]

Magnetic data for **11**–**13** are shown in Fig. 20 as μ_{eff} vs. T plots, which indicate that in all cases the magnetic behaviour is in general paramagnetic, although at the lowest temperatures a characteristic decrease of μ_{eff} for **11** and **13** is observed. The Weiss temperatures, calculated on the basis of inverse dependence of molar magnetic susceptibilities on temperature, $\theta = -1.037$, -0.191 and -0.99224 for **11**, **12** and **13** respectively, suggest weak antiferromagnetic interactions, probably due to Cu–Cu contacts, intrachain at a distance of $8.183(1)$ Å for **11** and interchain at a distance of $6.165(2)$ Å for **13** [20]. The room-temperature magnetic moment for each copper atom, ca. $1.8\mu_B$, is in the normal range for isolated $S = 1/2$ ions.

3. Heterotrimetallic complexes

As the reaction systems employed have been so productive in generating new heterobimetallic complex an attempt was undertaken to use the approach developed to obtain heterotrimetallic complexes (Table 2).

Table 2. Heterotrimetallic complexes obtained by direct synthesis [25, 26]

Initial system	Complex
$\text{Cu}^0\text{-CoCl}_2\text{-NiCl}_2\text{-HL}^2\text{-CH}_3\text{OH}$	$\text{Cu}_2\text{Ni}_2\text{Co}^{\text{II}}\text{Cl}_5(\text{L}^2)_5$ $\text{Cu}_2\text{Ni}_2\text{Co}^{\text{II}}\text{Cl}_4(\text{L}^2)_6$
$\text{Cu}^0\text{-CdCl}_2\text{-NiCl}_2\text{-HL}^2\text{-Solv}$ $\text{Solv} = \text{CH}_3\text{OH}, \text{CH}_3\text{CN}$	$\text{Cu}_2\text{Ni}_2\text{Cd}_2\text{Cl}_6(\text{L}^2)_6 \cdot 2\text{H}_2\text{O}$
$\text{Cu}^0\text{-CoX}_2\text{-ZnO-NH}_4\text{X-HL}^2\text{-CH}_3\text{OH}$ $\text{X} = \text{OAc}, \text{NCS}$	$\text{CuCo}^{\text{III}}\text{Zn}(\text{L}^2)_4(\text{NCS})_2\text{OAc}$
$\text{Cu}^0\text{-CoX}_2\text{-NiX}_2\text{-H}_2\text{L}^3\text{-CH}_3\text{OH}$ $\text{X} = \text{Cl}, \text{Br}, \text{OAc}, \text{NCS}, \text{HCOO}, \text{NO}_3$	$[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CuCo}^{\text{III}}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2\text{X}_2$ $\text{X} = \text{NCS}, \text{HCOO}, \text{NO}_3$ $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CuCo}^{\text{III}}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2\text{X}_2 \cdot 2\text{H}_2\text{O}$ $\text{X} = \text{Cl}, \text{Br}$
$\text{Cu}^0\text{-CoX}_2\text{-CdX}_2\text{-H}_2\text{L}^3\text{-CH}_3\text{OH}$ $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$	$[\text{CuCo}^{\text{III}}\text{Cd}(\text{H}_2\text{L}^3)_2(\text{L}^3)_2(\text{NCS})\text{X}_2] \cdot \text{CH}_3\text{OH}$ $\text{X} = \text{Cl}, \text{Br}$
$\text{Cu}^0\text{-CoCl}_2\text{-ZnCl}_2\text{-H}_2\text{L}^3\text{-CH}_3\text{OH}$	$[\text{Zn}_2\text{CuCo}^{\text{III}}(\text{L}^3)_3\text{Cl}_3(\text{CH}_3\text{OH})] \cdot \text{CH}_3\text{OH}$

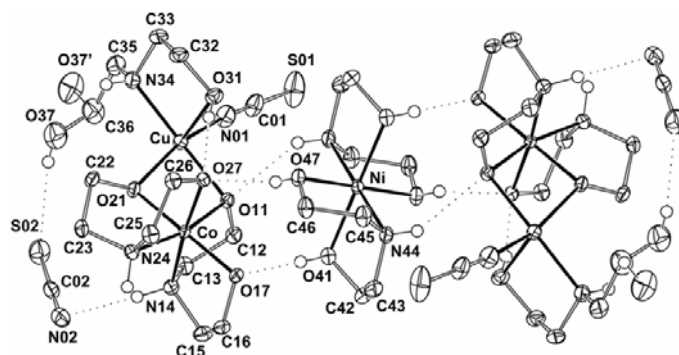


Fig. 21. The structure of the pentanuclear aggregate $\{[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2\}^{2+}$ in $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2(\text{NCS})_2$ and $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CuCo}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$ with the numbering scheme [25]

Three novel heterotrimetallic complexes $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2(\text{NCS})_2$ (**14**), $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CuCo}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (**15**) and $[\text{CuCoCd}(\text{H}_2\text{L}^3)_2(\text{L}^3)_2(\text{NCS})\text{Br}_2] \cdot \text{CH}_3\text{OH}$ (**16**) have been prepared using zerovalent copper, cobalt thiocyanate, nickel thiocyanate (**14**), nickel bromide (**15**) or cadmium bromide (**16**) and methanol solutions of diethanolamine in air. The overall structural configurations of isomorphous **14** and **15** [25] are similar with the uncoordinated NCS^- group in **14** replaced by disordered Br^- anion and water molecule in **15**. The molecular diagram and numbering scheme of **14** is shown in Fig. 21 which illustrates the general geometry of the two compounds. The most prominent feature of the structures of **14** and **15** is the formation of the “pentanuclear” aggregate $\{[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2\}^{2+}$ made up of two neutral $[\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]$ units and the cation $[\text{Ni}(\text{H}_2\text{L}^3)_2]^{2+}$, previously unknown. The Ni cation is on a crystallographic inversion centre, the Cu/Co moieties are situated on general positions. The presence of the molecular inversion

centre requires all five metal atoms to lie in the same plane. In the Cu–Co–Cu–Co parallelogram centred on Ni the bridged Cu...Co separations are of approximately 2.924 Å while other metal–metal distances vary from 4.640 to 5.328 Å.

The divalent nickel ion adopts a slightly distorted octahedral environment by interacting with two oxygen and two nitrogen atoms in the equatorial plane and two axially disposed oxygen atoms from two H_2L^3 ligands.

The metal atoms within $[\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]$ units are bridged by two oxygen atoms of two diethanolamine ligands. The copper(II) atom has distorted square-pyramidal coordination to a $\text{NO}_3\text{N}_{\text{NCS}}$ donor set. Each $[\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]$ unit is linked to the central Ni complex by two strong $\text{O}^-\cdots\text{H}\cdots\text{O}^-$ and one weaker $\text{N}^-\cdots\text{H}\cdots\text{O}^-$ charge-assisted hydrogen bonds, this arrangement producing eight-membered H-bonded rings (Fig. 21). Additional intermolecular association in the lattice occurs through the hydrogen bonding of the $\text{N}^-\cdots\text{H}\cdots\text{N}$, $\text{N}^-\cdots\text{H}\cdots\text{S}$, $\text{O}^-\cdots\text{H}\cdots\text{S}$ and $\text{N}^-\cdots\text{H}\cdots\text{Br}$ types involving thiocyanate groups (**14**) and bromide anions (**15**) to form 3-D frameworks (Fig. 22).

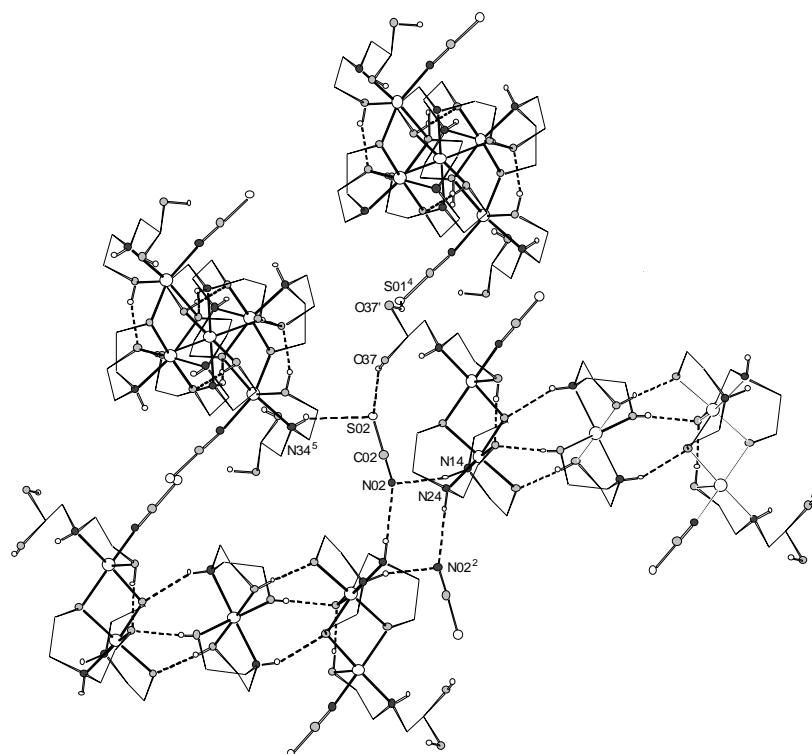


Fig. 22. View of $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2(\text{NCS})_2$ showing the hydrogen bonding network involving the uncoordinated thiocyanate anions [25]

X-ray crystallographic analysis of $[\text{CuCoCd}(\text{H}_2\text{L}^3)_2(\text{L}^3)_2(\text{NCS})\text{Br}_2]\cdot\text{CH}_3\text{OH}$ (**16**) [25] reveals an asymmetric three-metal atom core with metal atoms in a triangular array

(Fig. 23). With Cd^{2+} a different structure is obtained – the $[\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]$ unit is now linked to Cd centre through coordination of oxygen atoms of L^3 groups on the Co atom to form a discrete heterotrimetallic molecular species. The structural properties of the Cu/Co moiety are similar to those in **14** and **15** with Co atom being six-coordinate and Cu atom displaying a distorted square-pyramidal coordination. The geometry of the cadmium atom can be described as distorted octahedral with donor atoms of diethanolamine ligands and bromine atom.

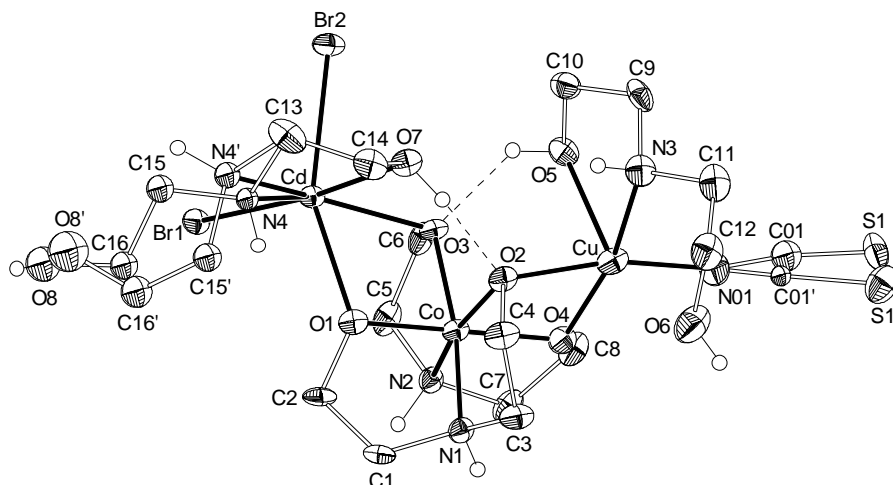


Fig. 23. Molecular structure of $[\text{CuCoCd}(\text{H}_2\text{L}^3)_2(\text{L}^3)_2(\text{NCS})\text{Br}_2]\cdot\text{CH}_3\text{OH}$ with the numbering scheme [25]

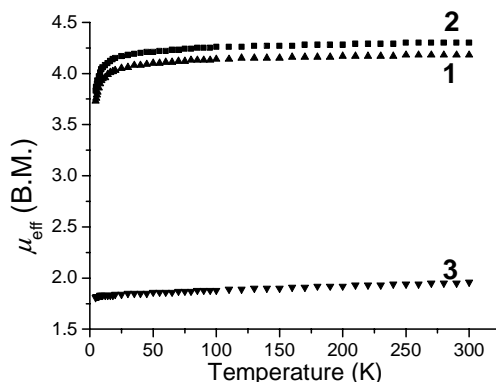


Fig. 24. Temperature dependences of the effective magnetic moment for $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CoCu}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2(\text{NCS})_2$ (1), $[\text{Ni}(\text{H}_2\text{L}^3)_2][\text{CuCo}(\text{L}^3)_2(\text{H}_2\text{L}^3)(\text{NCS})]_2\text{Br}_2\cdot 2\text{H}_2\text{O}$ (2) and $[\text{CuCoCd}(\text{H}_2\text{L}^3)_2(\text{L}^3)_2(\text{NCS})\text{Br}_2]\cdot\text{CH}_3\text{OH}$ (3) [25]

Experimental magnetic data for **14–16** are displayed in Fig. 24 as μ_{eff} vs. T plots. These show that in all cases the magnetic behaviour is paramagnetic [25]. On the as-

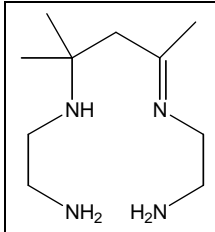
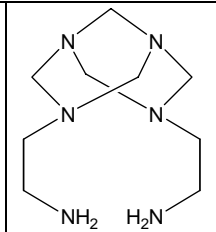
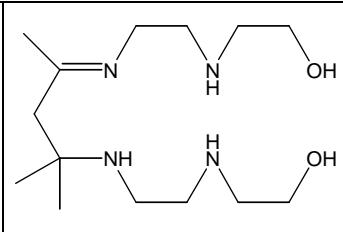
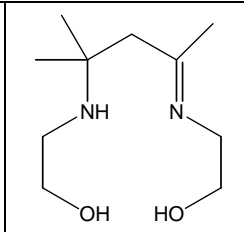
sumption that the Co^{3+} ions are diamagnetic, the room-temperature magnetic moment for **16**, 1.95 B.M., is typical of isolated $S = 1/2$ ions. The μ_{eff} values (per mole of complex) of the $\{\text{Cu}_2\text{Co}_2\text{Ni}\}$ complexes **14** and **15** are 4.18 and 4.3 B.M., respectively. Those are similar to the calculated value of 4.03 B.M. for a high spin $\text{Cu}_2^{\text{II}}\text{Ni}^{\text{II}}$ combination in which the constituent metals have typical μ_{eff} values of 1.9 and 3.0 B.M.

4. Direct template synthesis

Various solvents have been used to develop techniques of direct synthesis of heterobimetallic ethylenediamine complexes. Condensation of acetone with ethylenediamine resulted in the open-chain ligand, becoming the beginning of a new synthetic approach to heteropolynuclear complexes that we called “Direct template synthesis” (Table 3).

Table 3. Heterobimetallic complexes obtained by direct template synthesis [27, 28]

Initial system	Complex
$\text{Cu}^0\text{--M}^0\text{--en}\cdot n\text{HX--}(\text{CH}_3)_2\text{CO--Solv}$ $\text{M}^0 = \text{Zn, Mn}$ $\text{Ni}^0\text{--M}^0\text{--en}\cdot n\text{HX--}(\text{CH}_3)_2\text{CO--Solv}$ $\text{M}^0 = \text{Zn, Mn}$ $\text{X} = \text{Cl, Br, NCS}$ $\text{Solv} = \text{dmf, dmso, CH}_3\text{OH, CH}_3\text{CN}$	$[\text{CuL}^5\text{XZnX}_3]$ $\text{X} = \text{Cl, Br, NCS}$ $[\text{CuL}^5][\text{MnCl}_4]$ $[\text{NiL}^5][\text{ZnX}_4]$ $\text{X} = \text{Cl, Br, NCS}$ $[\text{NiL}^5][\text{MnX}_4]$ $\text{X} = \text{Cl, NCS}$
$\text{Co}^0\text{--ZnO--en}\cdot 2\text{HCl--}(\text{CH}_3)_2\text{CO--dmf}$	$[\text{Co}^{\text{III}}\text{L}^5\text{Cl}_2][\text{ZnCl}_3(\text{dmf})]$
$\text{Ni}^0\text{--K}_3[\text{Cr}(\text{NCS})_6]\text{--en}\cdot 2\text{HCl--}(\text{CH}_3)_2\text{CO--CH}_3\text{CN}$	$[(\text{NiL}^5)_6(\text{Cr}(\text{NCS})_6)_3]$ $[\text{Cr}(\text{NCS})_6]$
$\text{Ni}^0\text{--ZnO--en}\cdot 2\text{HX--NH}_4\text{X--CH}_2\text{O--Solv}$ $\text{X} = \text{Cl, Br}$ $\text{Solv} = \text{dmf, dmso}$	$[\text{NiL}^6][\text{ZnX}_4]$
$\text{M}^0(1)\text{--M}^0(2)\text{--amine}\cdot n\text{HCl--}(\text{CH}_3)_2\text{CO--Solv}$ $\text{M}^0(1) = \text{Ni, Cu; M}^0(2) = \text{Zn, Mn}$ $\text{Amine} = \text{N-(2-hydroxyethyl)-ethylenediamine, 2-aminoethanol}$ $\text{Solv} = \text{dmf, dmso, CH}_3\text{OH, CH}_3\text{CN}$	$[\text{M}(1)\text{L}^7][\text{M}(2)\text{Cl}_4]$ $[\text{CuL}^8\text{ZnCl}_3]_2$

			
L^5	L^6	L^7	HL^8

Complexes $[\text{CuL}^5\text{Zn}(\text{NCS})_4]$ (**17**) and $[\text{NiL}^5][\text{Zn}(\text{NCS})_4]$ (**18**) [27] have similar compositions and also similar crystal architecture. The $\text{M}(\text{L}^5)^{2+}$ and $\text{Zn}(\text{NCS})_4^{2-}$ ions can be seen as the main building blocks in both structures. In the case of **17** they are associated via the semi-coordinate $\text{Cu}\cdots\text{S}$ bond of 2.9 Å in a more robust “molecular” building block, $[\text{Cu}(\text{L}^5)\text{-}\mu\text{-SCNZn}(\text{NCS})_3]$ (Fig. 25). The building blocks $\text{M}(\text{L}^5)^{2+}$ and $\text{Zn}(\text{NCS})_4^{2-}$ are arranged in such a way that infinite helical chains form along the *a*-axis. The cations $\text{Cu}(\text{L}^5)^{2+}$ and $\text{Ni}(\text{L}^5)^{2+}$ are weakly bonded to the anionic chains through $\text{N-H}\cdots\text{S}$ hydrogen bonds and the semi-coordinate $\text{Cu}\cdots\text{S}$ bond of 2.9 Å in the case of **18**.

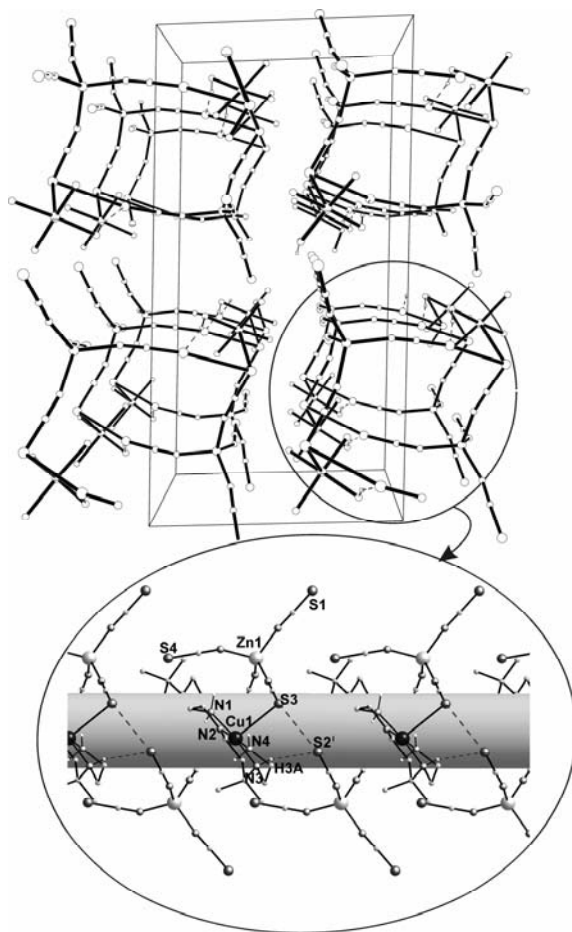


Fig. 25. Packing of helices in the crystal of $[\text{CuL}^5\text{Zn}(\text{NCS})_4]$ [27]

The nickel atom in $[\text{NiL}^6][\text{ZnCl}_4]$ (**19**) [27] (Fig. 26) has a square-planar environment being coordinated to four nitrogen atoms of the two ethylenediamine moieties of the ligand. The five-membered metal-chelate ring has the gauche conformation, and

the two six-membered rings have a chair conformation. The cations linked together via the N–H...N bond of 3.1 Å and 174° to form cationic chains. Those are further connected by $[\text{ZnCl}_4]^{2-}$ anions through the set of the linear Zn–Cl...H–N and cyclic Zn–Cl...H₂N motifs into a 2D net (Fig. 26).

The main structural blocks in the crystal of $[\text{Cu}(\text{L}^7)][\text{MnCl}_4]$ (**20**) are $[\text{Cu}(\text{L}^7)]^{2+}$ cations and $[\text{MnCl}_4]^{2-}$ anions (Fig. 27). The coordination environment of Cu(II) atom is formed by six (4N + 2O) donor atoms of L^7 . The geometry of $[\text{MnCl}_4]^{2-}$ is near tetrahedral, the average Cl–Mn–Cl bond angle being 109.5°. Hydrogen bonding seems to play an important role in the formation of the crystal lattice of **20**, taking into account the potential capacity of $[\text{Cu}(\text{L}^7)]^{2+}$ to act as a hydrogen donor and $[\text{MnCl}_4]^{2-}$ anion to act as a hydrogen acceptor. All of the five protons and all the chlorine atoms from the anion are involved in the N–H...Cl and O–H...Cl bonds (Fig. 27) [28].

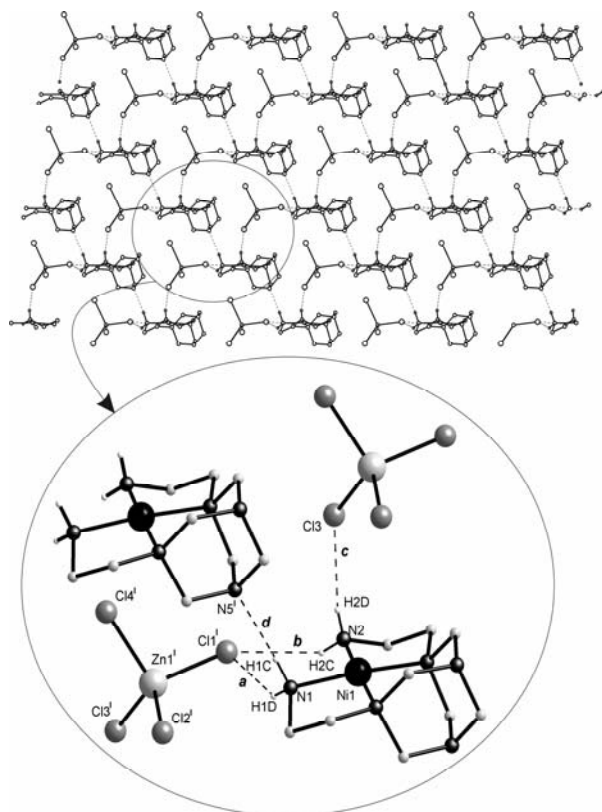


Fig. 26. The hydrogen bonded sheet of $[\text{NiL}^6][\text{ZnCl}_4]$ and its motif [27]

In contrast to the above mentioned compounds $[\text{Cu}(\text{L}^8)\text{ZnCl}_3]_2$ (**21**) [27] possesses a molecular (0D) framework (Fig. 28). Each molecule is a centrosymmetric dimer in which two $[\text{Cu}(\text{L}^8)\text{ZnCl}_3]$ halves can be distinguished. These halves are bound by long range, or semi-coordinate, Cu–Cl(1) bonds (2.728(2) Å) forming an eight-membered

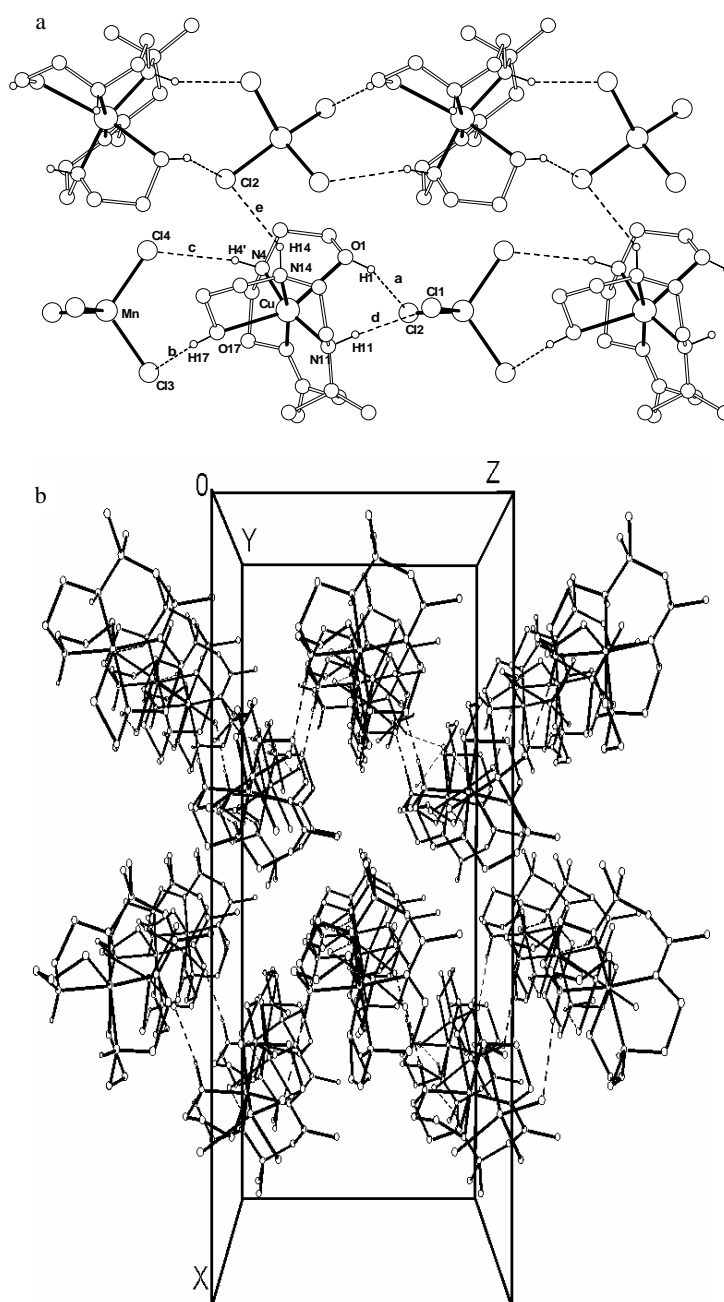


Fig. 27. Fragment of the layer in $[\text{CuL}^7][\text{MnCl}_4]$ with indication of H-bonds (a) and packing of the layers along the b axis (b) [28]

metallocycle based on a tetranuclear Zn_2Cu_2 skeleton with alternating metal and O/Cl atoms. The square-pyramidal coordination geometry around the copper centre is cre-

ated by 2N and 2O donor atoms from the monodeprotonated (L^8)⁻ ligand in the basal plane and chlorine atom Cl(1) occupying the axial position. The zinc atom (with $ZnCl_3O$ chromophore) adopts a very distorted tetrahedral symmetry. An interesting feature of the structure is the existence of two strong intramolecular H-bonds between neutral and deprotonated OH groups of L^8 (with the O...O distance of ca. 2.5 Å) which form an additional 8-membered ring joining copper atoms inside the dimer molecule.

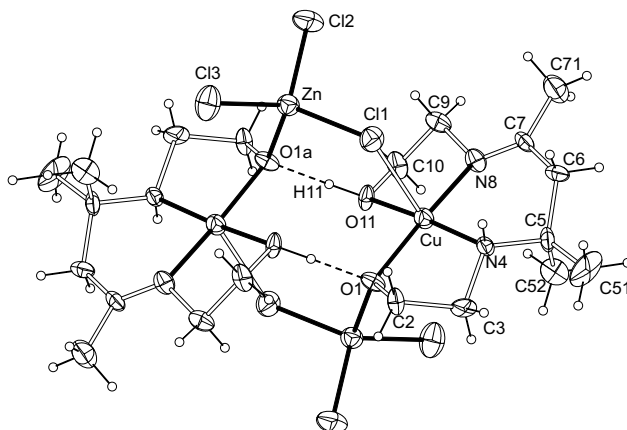
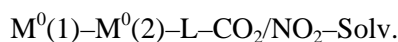


Fig. 28. Molecular structure of $[CuL^8ZnCl_3]_2$ with the numbering scheme [27]

A large amount of compounds that can participate in condensation reactions promises new advances in the field of direct template synthesis.

5. Conclusion

This paper describes novel synthetic routes to heteropolynuclear complexes developed using simple starting materials and relatively mild reaction conditions. Well-known classic acidoligands – carbonate and nitrate – have been of much interest recently as building blocks for the construction of coordination polymers. For example, carbonate group can act even as a μ_6 -bridge [29]. Heteropolynuclear complexes with these anions have to form in conditions of direct synthesis as well, for example, in the systems:



It is hoped that this synthetic approach will be profitable in obtaining novel heteropolynuclear complexes with various nuclearity and dimensionalities.

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