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Design of Cyano-Bridged Coordination Polymers Based on Tetrahedral Rhenium Cluster Cyanide Complexes and 3d Transition Metals

Olga A. Efremova,[a] Yuri V. Mironov,*[a] and Vladimir E. Fedorov[a]

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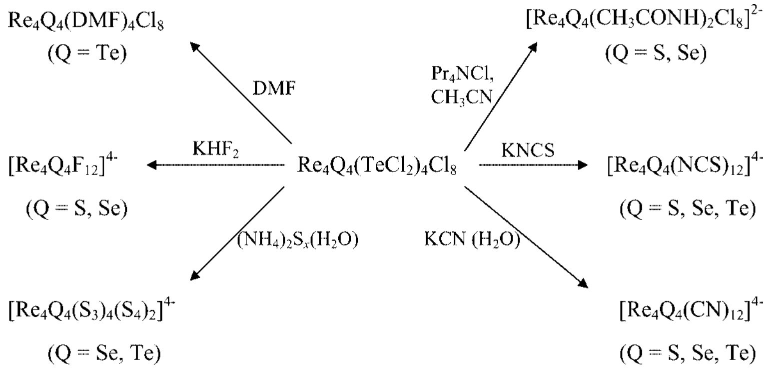
This microreview surveys some novel possibilities in the design of coordination polymers using the tetrahedral rhenium cluster chalcocyanide complexes $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) and 3d transition metals. The large number of cyano groups in the cluster complexes $[Re_4Q_4(CN)_{12}]^{4-}$, their ambidentate character and their strong ability to form cyano-bridged structures lead to the formation of a wide variety of coordination polymers with different architectures that depend on the reaction conditions. The diversity of the coordination environment of the transition metals has been used as one of the most important factors to control the dimensionality of the crystal structures of the target compounds.

1. Introduction

Tetranuclear cluster complexes are well known for most of the transition metals.[1–4] These compounds contain the M_4Q_4 cluster core as the main structural fragment, which can be represented as two interpenetrating M_4 and Q_4 tetrahedra. In these M_4Q_4 cluster cores, the inner μ_3-Q ligands are most often chalcogenide ions. In this paper we will review only those tetrahedral rhenium cluster chalcocyanide complexes that have the stoichiometry $[Re_4Q_4(CN)_{12}]$ (Q = S^{2-}, Se^{2-} and Te^{2-}) where each rhenium atom is additionally coordinated by three outer-sphere CN ligands. Within the framework of the ion-covalent model the formal oxidation state of rhenium in similar clusters is 4+ (the d^3 configuration), therefore there are six covalent metal–metal bonds in the Re_4 tetrahedron (two electrons for each edge of the tetrahedron).

Significant progress in the developing chemistry of Re_4 cluster compounds was achieved after synthesis of the chalcogenide-halide clusters $[Re_4Q_4(TeX_2)_4X_8]$ (Q = S, Se, Te; X = Cl;[5] Q = Te, X = Br[6]). The tellurium-containing complex $[Re_4Te_4(TeCl_2)_4Cl_8]$ was prepared by the reaction of $ReCl_5$ with elemental tellurium at 350 °C. Complexes with Q = S and Se were synthesised by the reaction of $ReCl_5$ with mixtures of elemental tellurium and sulfur or selenium, respectively, at 400 °C.



Scheme 1.

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[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3, Acad. Lavrentiev pr., 630090 Novosibirsk, Russia
Fax: +7-383-330-9489
E-mail: yuri@che.nsk.su

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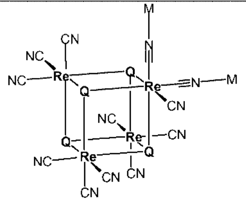
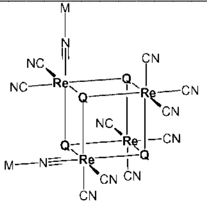
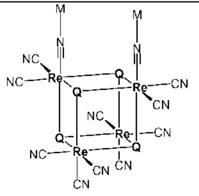
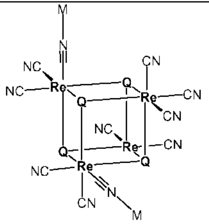
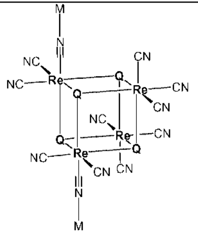
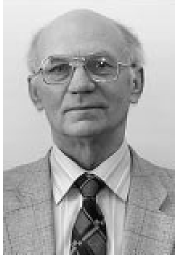
Table 1. Labels for the CN ligand couples taking part in binding with transition metal cations.

Label	Binding type	Label	Binding type
gem-CN groups		*ortho*-CN groups	
sym-CN groups		*meta*-CN groups	
		para-CN groups	

Olga Efremova graduated from the Natural Science Department of the Novosibirsk State University in 2005. Because of her excellent academic record during her education at the University she was awarded several Fellowships. Her diploma work was devoted to the synthesis and study of the structure and properties of coordination polymers based on tetrahedral chalcocyanide rhenium cluster complexes. At present, Olga is working in the group of Prof. Yuri Mironov in the Laboratory of Prof. Fedorov (Nikolaev Institute of Inorganic Chemistry, Russian Academy of Sciences) where she is continuing her experimental studies as a PhD student. Her current research is devoted to the development of different approaches to the design of nanomaterials with different dimensionalities using cluster anionic complexes and 3d or 4f transition metal cations possessing tailored ligand environment as building blocks. She teaches students of the Natural Science Department of NSU.

Yuri Mironov graduated from the Natural Science Department of the Novosibirsk State University in 1981 and received his PhD from the Institute of Inorganic Chemistry of the Russian Academy of Sciences in 1990. In 2000 he received his highest scientific degree – Doctor of Chemical Sciences – and habilitated as Professor of Chemistry. He is an experienced researcher in coordination and cluster chemistry. His research interests cover the realm of synthesis, reactivity, structures and properties of cluster halides, chalcogenides and chalcohalides of the early transition metals (V, Nb, Mo, W, Re). Prof. Mironov and his students have synthesised and characterised more than two hundred new cluster compounds and published about a hundred articles. He has been awarded several grants from different foreign foundations, like the Alexander von Humboldt Foundation (with Prof. W. S. Sheldrick, Bochum University, Germany) and the NSF (with Prof. J. A. Ibers, Northwestern University, USA), and has also received a Korean Fellowship (with Prof. S.-J. Kim, Ewha Womans University, Seoul, Korea).



Vladimir Fedorov graduated from the Leningrad Institute of Technology and obtained his Dipl. Ing. in 1959. The same year he went as an engineer to the plant of advanced ceramics and composites in Novosibirsk where he spent three years. From 1963 to 1966 he studied inorganic, coordination and solid-state chemistry at the Natural Science Department of the Novosibirsk State University, where he completed his thesis and received his PhD. From 1966 to the present day V. Fedorov has been working at the Nikolaev Institute of Inorganic Chemistry, Russian Academy of Sciences (Novosibirsk). Further research in cluster chemistry led to the award of his highest scientific degree – Doctor of Chemical Sciences – in 1990. He then habilitated the position of Full Professor of Inorganic Chemistry. Currently he is head of the laboratory of synthesis of cluster compounds and materials and a lecturer at the Natural Sciences Department of the Novosibirsk State University, where he teaches cluster chemistry of the transition metals. The main research interests of Prof. Fedorov lie in cluster, coordination and medical chemistry, including the synthesis and design of materials, the study of crystal and electronic structures, and the investigation of different physico-chemical properties of solids and solutions. Prof. Fedorov's studies have resulted in more than 350 scientific publications, two monographs and several patents.

The $[Re_4Q_4(TeCl_2)_4Cl_8]$ compounds are insoluble both in water and common organic solvents but readily react with various compounds in aqueous solution or organic solvents or even with the solvents themselves upon heating or occasionally at room temperature. All such transformations proceed with the replacement of the outer-sphere ligands ($TeCl_2$ or Cl^-) of the cluster complexes, resulting in the formation of compounds with different outer ligands (fluoride, polysulfide, thiocyanate, cyanide, acetamide, DMF etc.; see Scheme 1).[7–12]

The cyanide complexes $[Re_4Q_4(CN)_{12}]^{4-}$ are of particular interest among these compounds. Due to their ambidentate character, the CN groups can serve as bridging ligands to give polymeric compounds of different dimensionalities. Such an approach has been applied for the preparation of coordination polymers based on Re_6[13–19] cluster chalcocyanides and very recently was successfully used for W_6[20] and Nb_6[21–22] cyano complexes. Re_4 cluster complexes have 12 CN ligands (three for each Re atom), in contrast to the six CN ligands (one for each Re atom) in M_6 cluster complexes. This difference leads to a greater variety of coordination complexes of Re_4 chalcocyanides with transition metals. In recent years, we have carried out systematic studies of the synthesis of cyano-bridged coordination polymers based on the tetrahedral rhenium cluster complexes $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se or Te) and 3d metal complexes. The use of polydentate ligands in the coordination sphere of transition metals offers additional possibilities for controlling the dimensionality of the resulting cyano-bridged compounds.

For the convenience of structure description in cases where two transition metal cations are coordinated by one cluster anion we offer the following labels for the CN ligand couples that take part in binding (Table 1).

One of the important experimental factors for the reactions mentioned below is the reaction medium. The compounds described in this review were obtained either in aqueous solution or in aqueous ammonia solution.

2. The Interaction of $[Re_4Q_4(CN)_{12}]^{4-}$ Anions with Aqua Complexes of Transition Metals

The reaction of water solutions of $K_4[Re_4Te_4(CN)_{12}]$ and $CuCl_2$ in a gel based on sodium silicate leads to the cluster complex $[Cu_4(\mu_3\text{-}OH)_4][Re_4(\mu_3\text{-}Te)_4(CN)_{12}]$ (**1**).[23] The structure of this compound contains layers built up from tetranuclear $[Cu_4(\mu_3\text{-}OH)_4]^{4+}$ cations and $[Re_4Te_4(CN)_{12}]^{4-}$ cluster anions (Figure 1). Eight of the twelve CN^- ligands of the cluster anion coordinate copper atoms in the layer; the four remaining CN^- ligands are directed perpendicular to the layer and are bonded to the OH groups of cations from adjacent layers. In the $[Cu_4(\mu_3\text{-}OH)_4]^{4+}$ cation, which is synthesised by a self-assembly reaction, the four copper atoms and four OH^- groups form a cubane-like structure with two short and four long Cu–Cu distances of 2.99 and 3.18 Å, respectively.

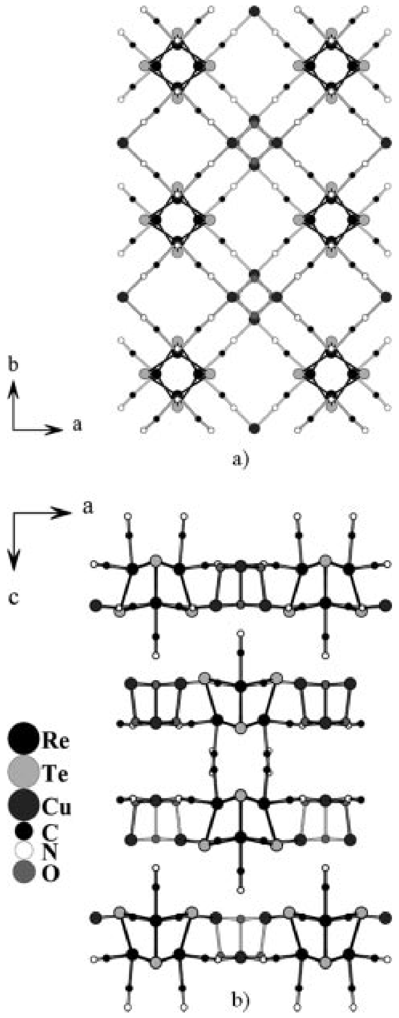


Figure 1. a) The covalent layer in **1** (projection along the *ab* plane). b) The packing of the layers (projection along the *ac* plane). Hydrogen atoms have been omitted for clarity in this figure and others.

If the reaction of $K_4[Re_4Te_4(CN)_{12}]$ and $CuCl_2$ is carried out in 1 M hydrochloric acid solution the three-dimensional cluster complex $[\{Cu(H_2O)_2\}\{Cu(H_2O)_2\}Re_4Te_4(CN)_{12}]$ (**2**) is formed.[11] There are two copper cations with different coordination environments in the structure of this compound. The Cu1 cation is coordinated by four nitrogen atoms of CN groups and by two oxygen atoms of water molecules to form a two-dimensional network in which the cluster units are linked through Re–C≡N–Cu–N≡C–Re bridges, whereas the Cu2 cation is coordinated by two nitrogen atoms of CN groups and two oxygen atoms of water molecules to give a square-planar environment of the Cu2 atoms (Figure 2). The Cu2 cation bridges two-dimensional networks to give a complicated three-dimensional packing.

The ions Cd^{2+} and Mn^{2+} give two related cluster complexes, namely $[\{Cd(H_2O)_2\}\{Cd(H_2O)_4\}Re_4Te_4(CN)_{12}]$ (**3**) and $[\{Mn(H_2O)_2\}\{Mn(H_2O)_4\}Re_4Te_4(CN)_{12}]$ (**4**).[11] They are isostructural to the copper complex **2** although, unlike the Cu2 cation, Cd2 and Mn2 demand an octahedral environment. Such a coordination preference results in disordering of the M2 cations over two crystallographically

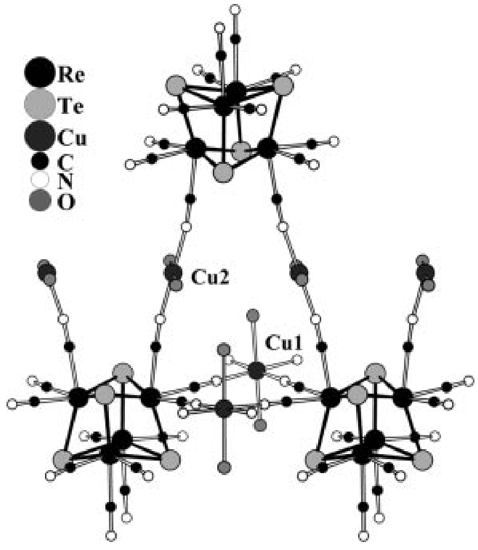


Figure 2. A fragment of the crystal structure of compound **2**.

equivalent positions with equal contributions in complexes **3** and **4**. This cation is coordinated by two nitrogen atoms of CN groups and four oxygen atoms of water molecules. M2–M2 dimers are present in the structure, with two water molecules and a cluster anion coordinated as bridges (Figure 3).

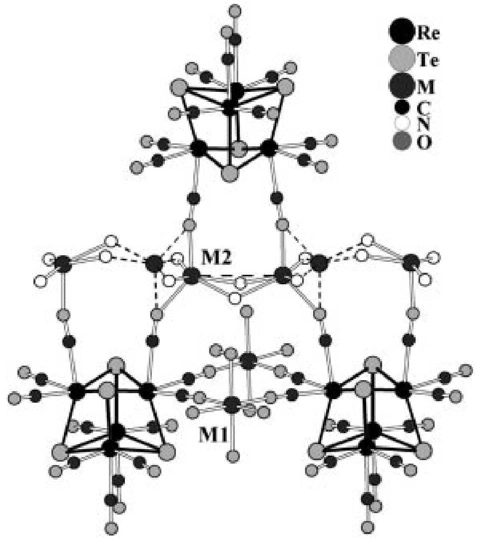


Figure 3. The M(2)···M(2) dimers in the structures of **3** and **4**. The second, disordered positions of M(2) are shown by dashed bond lines.

3. The Interaction of $[Re_4Q_4(CN)_{12}]^{4-}$ Anions with Amino Complexes of Transition Metals

The interaction of cluster anions with amino complexes of metal cations such as Ni^{2+}, Cd^{2+} and Cu^{2+} gives different products to those obtained with aqua complexes.

The compound $[\{Ni(NH_3)_5\}_2\{Re_4Te_4(CN)_{12}\}]\cdot 3.4H_2O$ (**5**) was prepared from $NiCl_2$ and $K_4[Re_4Te_4(CN)_{12}]$ in aqueous ammonia solution.[24] The molecular structure of this compound contains two $[Ni(NH_3)_5]^{2+}$ cations bonded to one cluster anion through the nitrogen atoms of the *gem*-CN groups. The coordination polyhedron of the Ni atoms is practically a regular octahedron (Figure 4).

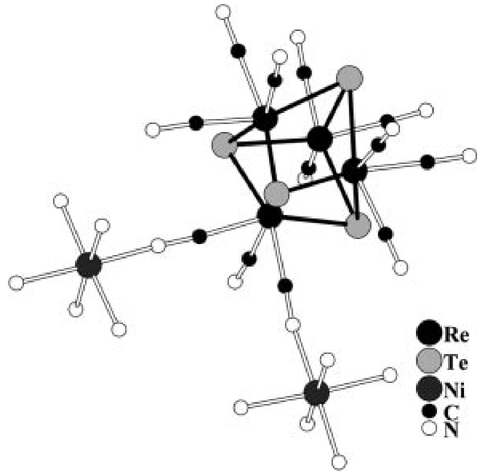


Figure 4. View of the $[\{Ni(NH_3)_5\}_2Re_4Te_4(CN)_{12}]$ molecule in **5**.

The use of $CdSO_4$ instead of $NiCl_2$ leads to the formation of a compound formulated as $[\{Cd(NH_3)_5\}\{Cd(NH_3)_3\}\{Re_4Te_4(CN)_{12}\}]\cdot 4H_2O$ (**6**).[24] This compound contains two types of cations: a terminal $[Cd(NH_3)_5]^{2+}$ cation and a bridging $[Cd(NH_3)_3]^{2+}$ one. Whereas the $[Cd(NH_3)_5]^{2+}$ cations are coordinated by only one cyanide group, the $[Cd(NH_3)_3]^{2+}$ cations are coordinated by three CN groups of different cluster anions to form a chain-like structure (Figure 5).

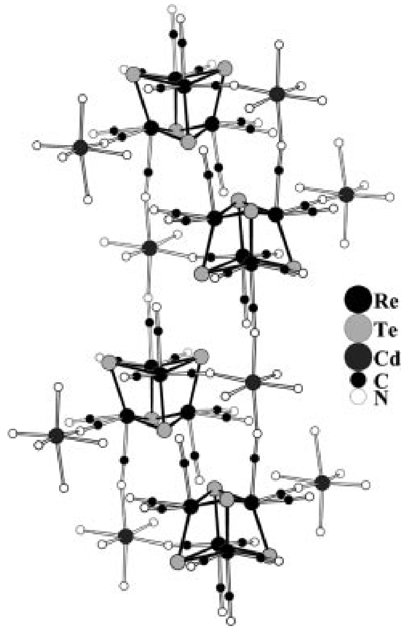


Figure 5. A fragment of the crystal structure of **6**.

The reaction of aqueous $K_4[Re_4Q_4(CN)_{12}]$ solutions with an ammonia solution of $CuCl_2$ give the complexes $[\{Cu(NH_3)_3\}_2\{Re_4Q_4(CN)_{12}\}]\cdot nH_2O$ [Q = S (**7**), Se (**8**)] (Figure 6) and $[\{Cu(NH_3)_3\}_{1.7}\{Cu(NH_3)_4\}_{0.3}Re_4Te_4(CN)_{12}]$

(**9**).[25] In compounds **7** and **8** the $[Re_4Q_4(CN)_{12}]^{4-}$ cluster units are linked by cyanide bridging ligands through $[Cu(NH_3)_3]^{2+}$ to give chains that extend along the *c* axis. In the case of Q = Te these chains have a discrete character because some of the copper atoms are coordinated by four ammonia molecules (Figure 7). These copper cations have a distorted square-pyramidal coordination environment formed by three ammonia molecules and the N atom of the CN ligand in the equatorial plane, and additionally by the N atom of the CN ligand in the apical position.

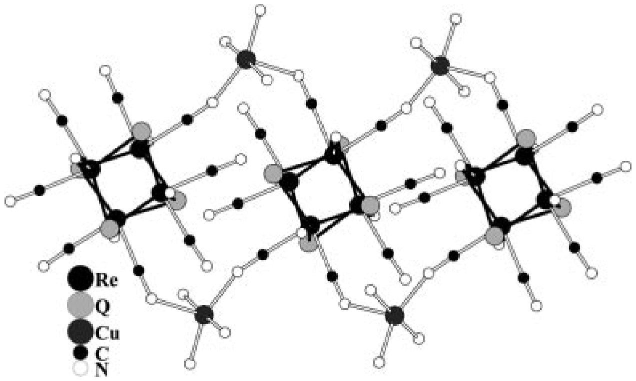


Figure 6. A fragment of the crystal structure of compound **7**.

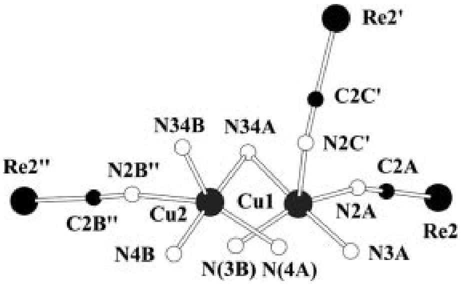


Figure 7. Disordering of the Cu atoms over two positions in the crystal structure of compound **9**.

Compounds **7**–**9** have a one-dimensional topology similar to **6**. However, there are several differences. For instance, the Cd atoms have an octahedral coordination environment whereas the Cu atoms have a square-pyramidal environment, and in **6** only half of the Cd atoms are bridged linking three clusters at once.

The reaction of an aqueous $K_4[Re_4Te_4(CN)_{12}]{\cdot}5H_2O$ solution with a $ZnCl_2$ ammonia solution leads to formation of $[\{Zn(H_2O)_2\}\{Zn(H_2O)_4\}Re_4Te_4(CN)_{12}]$ (**10**), which has a structure similar to that of compounds **3** and **4**. Compound **10** dissolves when ammonia is added and can be recrystallised by removing this ammonia.[26]

Thus, the formation of compounds **5**–**9** can be considered as stages in the formation of **2**–**4**. In this scheme, the polymeric complex **10** is the final product.

4. The Interaction of $[Re_4Q_4(CN)_{12}]^{4-}$ Anions with Amino Complexes of Transition Metals in the Presence of Polydentate N-Donor Ligands

One of the most convenient and effective ways to change the dimensionality of structures is by using polydentate ligands, which can effectively block coordination sites around the transition metal cations and thus control the number of coordination sites available for binding with CN groups. Partial or complete blocking of coordination sites allows the directional regulation of structure dimensionality. A wide assortment of polydentate ligands having N-donor atoms, such as ethylenediamine (en), diethylenetriamine (dien), triethylenetetraamine (trien) and *threo*-tetraaminobutane (*threo*-tab), have been used for such a purpose. These ligands can block two, three or four coordination sites around the transition metal, and also can behave as bridges.

4.1. Complexes with Ethylenediamine

The interaction of M^{2+} transition metal cations having different coordination numbers [*n* = 6 (Ni, Zn, Cu) and 5 (Cu)] with bidentate ethylenediamine in water or aqueous ammonia solution leads to the formation of complexes with different M/en ratios. This can be described by the stepwise complex formation shown in Equations (1), (2) and (3) (L = H_2O, NH_3).

$$[ML_n]^{2+} + en \rightarrow [ML_{n-2}(en)]^{2+} + 2\,L \tag{1}$$

$$[ML_{n-2}(en)]^{2+} + en \rightarrow [ML_{n-4}(en)_2]^{2+} + 2\,L \tag{2}$$

$$[ML_{n-4}(en)_2]^{2+} + en \rightarrow [M(en)_3]^{2+} + 2\,L \tag{3}$$

Generally, all cationic forms coexist simultaneously in solution and can interact with cluster anions to give compounds of different stoichiometry. The predominance of one form or another depends on the ligand concentration, i.e. the M/en ratio in solution, and the stability constants of the corresponding complexes; the form that reacts with the cluster anion to give the solid depends on these factors and its solubility too.

4.1.1. Compounds Containing $[Ml_{n-2}(en)]^{2+}$

The interaction of $K_4[Re_4Se_4(CN)_{12}]$ with an equimolar mixture of $CuCl_2$ and en in aqueous ammonia solution leads to the formation of $[\{Cu(en)\}\{Cu(NH_3)(en)\}$-$Re_4Se_4(CN)_{12}]{\cdot}5H_2O$ (**11**)[27] in which the chemical form $[CuL_3(en)]^{2+}$ (L = CN and NH_3; *n* = 5) is observed. There are two copper cations in the structure of this compound, both of which have a distorted square-pyramidal environment but different coordination compositions. The Cu1 cation is coordinated by two amino groups of an en molecule and three nitrogen atoms of CN ligands of different cluster anions, whereas Cu2 bridges only two cluster anions so it is coordinated by two N atoms of CN ligands, en and ammonia molecules. As a result this compound has a complicated polymeric structure in which two infinite chains directed along *b* axes are linked through Re–CN–Cu1 bridges (Figure 8).

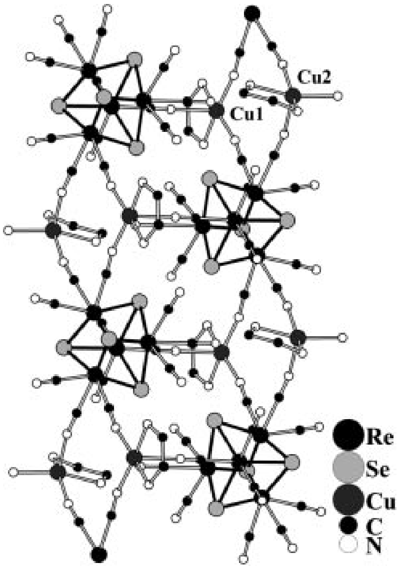


Figure 8. A fragment of the structure of complex **11**.

4.1.2. Compounds Containing a Mixture of $[ML_{n-2}(en)]^{2+}$ and $[ML_{n-4}(en)_2]^{2+}$

A mixture of chemical forms corresponding to the first and the second steps of complex formation, in a 1:1 ratio, was observed in complexes $[Ni(NH_3)_4(en)][\{Ni(NH_3)(en)_2\}Re_4Te_4(CN)_{12}]\cdot 2H_2O$ (**12**) and $[Zn(NH_3)_2(en)_2][\{Zn(NH_3)_2(en)\}Re_4Te_4(CN)_{12}]\cdot H_2O$ (**13**) (L = NH_3 and CN).

Compound **12** was obtained from an aqueous ammonia solution containing $K_4[Re_4Te_4(CN)_{12}]$, $NiCl_2$ and ethylenediamine (Ni/en ratio of 1:1.5).[28] The structure of **12** is ionic, with an $[Ni(NH_3)_4(en)]^{2+}$ cation and an $[\{Ni(NH_3)(en)_2\}Re_4Te_4(CN)_{12}]^{2-}$ anion (Figure 9). The $[Ni(NH_3)_4(en)]^{2+}$ cation corresponds to the $[ML_{n-2}(en)]^{2+}$ chemical form in Equation (1) for an octahedral environment. At the same time, the $[\{Ni(NH_3)(en)_2\}Re_4Te_4(CN)_{12}]^{2-}$ anion can be described as the result of substitution of an ammonia molecule by the $[Re_4Te_4(CN)_{12}]^{4-}$ cluster anion in the coordination environment of a *cis*-$[Ni(NH_3)_2(en)_2]^{2+}$ complex cation.

Compound **13** also has an ionic structure, with an *cis*-$[Zn(NH_3)_2(en)_2]^{2+}$ cation corresponding to the $[ML_{n-4}(en)_2]^{2+}$ (n = 6) chemical form and a $[\{Zn(NH_3)_2(en)\}Re_4Te_4(CN)_{12}]_n^{2n-}$ anion, which has a zigzag chain-like structure (Figure 10).[26] Once again, the anion formation can be viewed as the result of substitution of *cis*-ammonia molecules by nitrogen atoms of two different cluster anions in the $[ML_{n-2}(en)]^{2+}$ chemical form.

It should be noted that only these two compounds out of the whole series of tetrahedral rhenium cluster complexes including $[ML_{n-4}(en)_2]^{2+}$ units contain *cis*-$[ML_2(en)_2]^{2+}$ cations. An analysis of the structural data of all compounds deposited in the CCDC (CSD v.5.25) shows that the number of *trans*-$[ML_2(en)_2]^{2+}$ complexes is much higher than that of *cis*-$[ML_2(en)_2]^{2+}$ complexes. Apparently, *trans*-$[ML_2(en)_2]^{2+}$ complexes are energetically more stable than the *cis*-$[ML_2(en)_2]^{2+}$ form. However, the isolation of this form from solution has proved to be possible upon crystallisation with cluster anions.

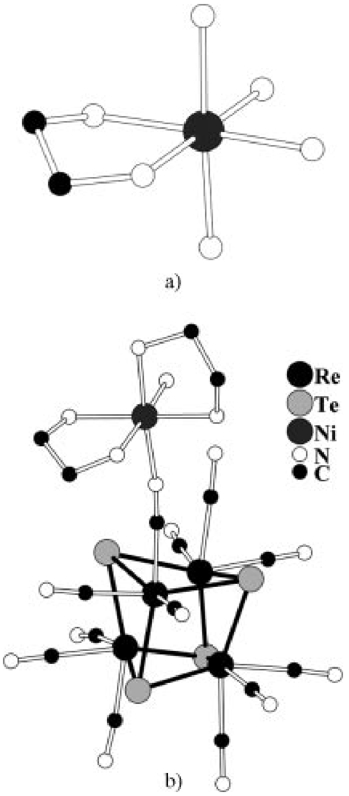


Figure 9. Structure of the complex $[Ni(NH_3)_4(en)]^{2+}$ cation (a) and the $[\{Ni(NH_3)(en)_2\}Re_4Te_4(CN)_{12}]^{2-}$ anion (b) in compound **12**.

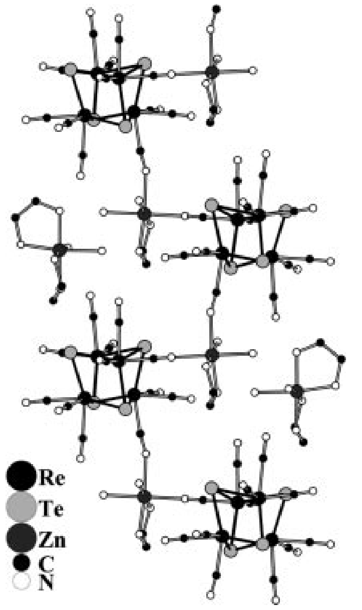


Figure 10. A fragment of structure of **13**.

4.1.3. Compounds Containing Only $[ML_{n-4}(en)_2]^{2+}$

All compounds synthesised in the presence of ethylenediamine with an M/en ratio of 1:2 contain *trans*-$[ML_{n-4}(en)_2]$ units. Such complexes are known with bridging $\{M(en)_2\}$

(M = Ni^{2+}, Cu^{2+} and Zn^{2+}) groups or terminal $\{Cu(en)_2\}$ (n = 5) groups coordinated to CN ligands of the cluster anion.

The compound $[\{Cu(en)_2\}_2Re_4S_{3.83}Te_{0.17}(CN)_{12}]\cdot H_2O$ (**14**) has a polymeric grid structure in which the $[Re_4S_{3.83}Te_{0.17}(CN)_{12}]^{4-}$ cluster anions are situated at the cross-points of this lattice and are linked by $[Cu(en)_2]^{2+}$ cationic units, as depicted in Figure 11. Each Cu atom in the cationic part has a [4+2] coordination environment: it is coordinated by four NH_2 groups of two ethylenediamine units in the equatorial plane and by two N atoms of CN ligands of different cluster anions with longer Cu–N distances (2.367 and 2.759 Å).[29]

The isostructural compounds $[\{Ni(en)_2\}_2Re_4Se_4(CN)_{12}]\cdot 3.25H_2O$ (**15**)[18] and $[\{Zn(en)_2\}_2Re_4S_{3.60}Te_{0.41}(CN)_{12}]\cdot 3.75H_2O$ (**16**)[29] have a polymeric grid structure with $[Re_4Q_4(CN)_{12}]^{4-}$ cluster anions at the cross-points and $[M(en)_2]^{2+}$ moieties on the edges (Figure 12). However, two of these lattices are arranged differently. In the case of **14** four CN groups of two rhenium atoms (2+2) take part in binding; whereas in of **15** and **16** four CN ligands belonging to three Re atoms (2+1+1) of the cluster anion are involved in formation of the polymeric structure. In this context, the different bridging modes have a crucial influence on the packing characteristics. The bent bridging modes in **14** result in the formation of wavy layers (Figure 13, a), whereas the tentatively flat binding of **15** and **16** generates approximately planar layers (Figure 13, b).

The compound of composition $[Ni(NH_3)_2(en)_2][\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]\cdot 38H_2O$ (**17**) was obtained under the same reaction conditions as those of **15**. However, the structure of this compound differs dramatically. Figure 14 shows the structure of the $[\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]^{2-}$ anion, in which $[Re_4Te_4(CN)_{12}]^{4-}$ clusters are linked by $\{Ni(en)_2\}^{2+}$ units to form hexagonal layers. There are two types of channels in this structure: large hexagonal and smaller triangular ones, which are filled with water molecules and $[Ni(NH_3)_2(en)_2]^{2+}$ counterions. The volume of the large cavity is 1590 Å^3 and the volume of each of the two smaller ones is 640 Å^3. The total available volume for solvent per unit cell is 2870 Å^3, corresponding to about 37% of the unit cell volume. Compound **17** is the first example of a highly porous structure derived from the tetrahedral Re_4Q_4 cluster core. The en molecules coordinated to the Ni atoms make the framework in **17** robust and prevent its collapse after dehydration. Indeed, powder diffraction studies of samples left in air for weeks at room temperature and after heating to 120 °C (a temperature at which the material is completely dehydrated according to thermal analysis) indicate that the original crystal structure remains essentially unchanged. The walls of the large channels of the framework in **17** are decorated by twelve N atoms from the terminal CN ligands of the $[Re_4Te_4(CN)_{12}]^{4-}$ cluster anion in every sheet. This feature makes this robust framework an attractive matrix for inclusion of molecules or ions of corresponding size and shape based on “host–guest” prin-

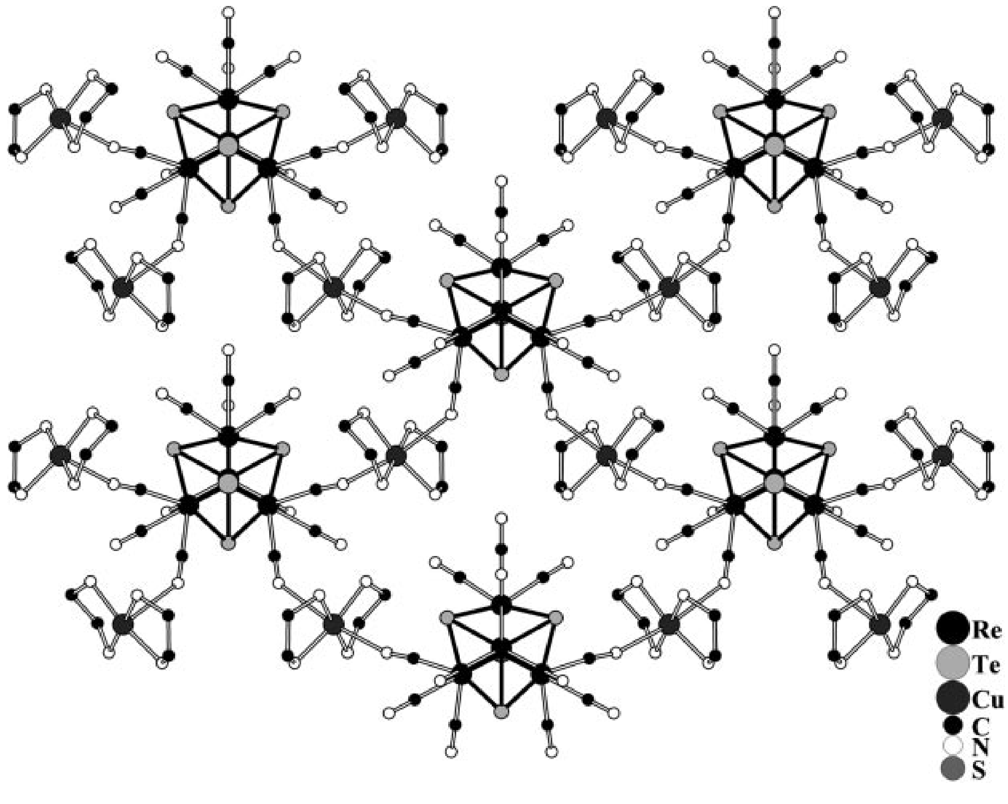


Figure 11. A fragment of the layer in compound **14**.

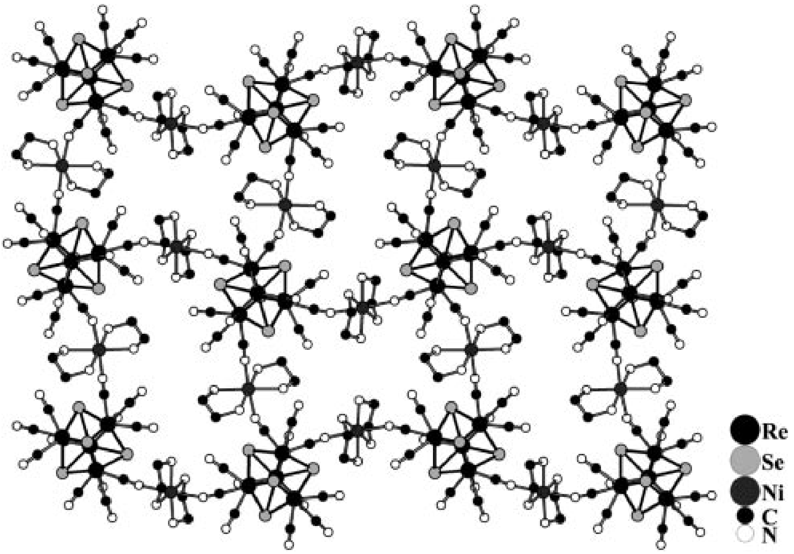


Figure 12. A fragment of the layer in compound **15**.

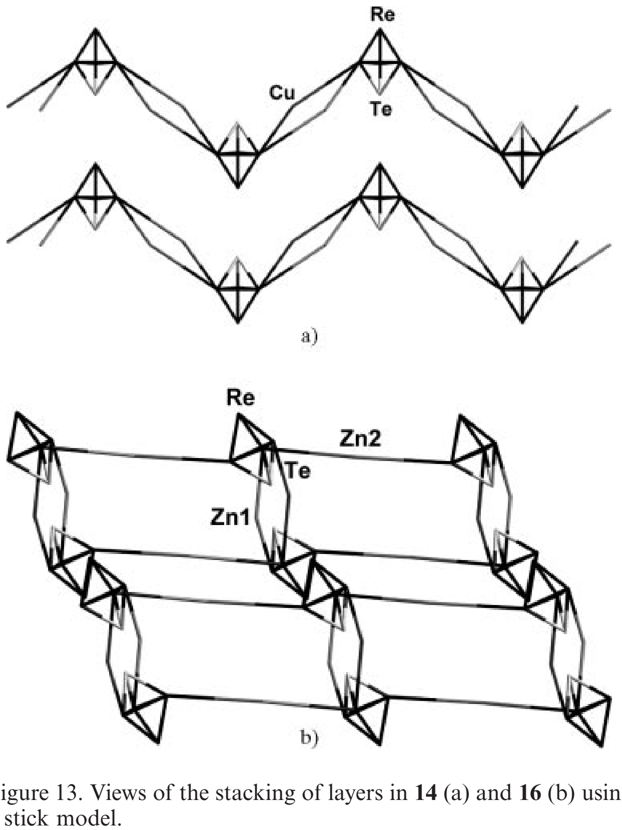


Figure 13. Views of the stacking of layers in **14** (a) and **16** (b) using a stick model.

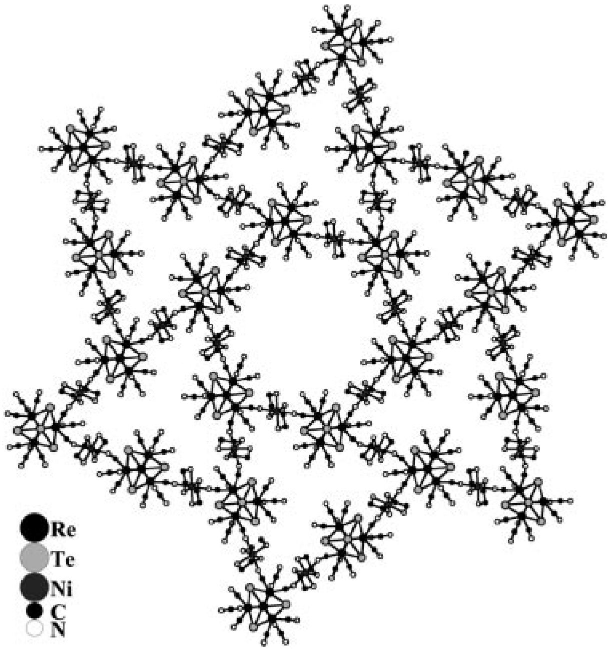


Figure 14. View down the *c* axis of the crystal packing of the $[\{Ni(en)_2\}_3\{Re_4Te_4(CN)_{12}\}_2]^{2-}$ polymeric anion in **17**.

ciples. The N atoms directed into the channel are able to form both covalent bonds, with any N-acceptor atoms such as transition metals, and hydrogen bonds, with H-containing molecules such as alcohols, to guest molecules.[30] Apparently, the reason for formation of such differently arranged structures as that of **15** and **17** is the different cluster core composition (Re_4Se_4 in **15** and Re_4Te_4 in **17**).

The use of $[Cu(en)_2Cl_2]$ instead of $[Ni(en)_2Cl_2]$, which was used for the synthesis of **15** and **17**, gives the formation of the molecular compounds $[\{Cu(en)_2\}_2Re_4Q_4(CN)_{12}]\cdot5H_2O$ [Q_4 = Te_4 (**18**),[31] STe_3 (**19**)[32]], which have different structures. In these compounds the $[Re_4Q_4(CN)_{12}]^{4-}$ cluster anions are coordinated by two $\{Cu(en)_2\}^{2+}$ units in opposite directions (Figure 15). To put it another way, every *trans*-$\{Cu(en)_2\}$ unit is linked to only one CN ligand of the cluster anion, which means that *n* in this case is equal to 5; this results in the formation of a molecular structure.

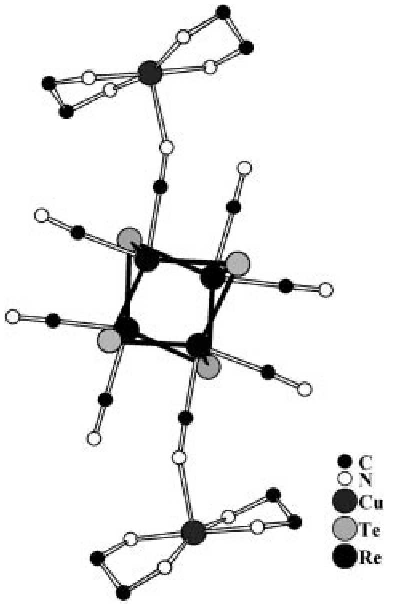


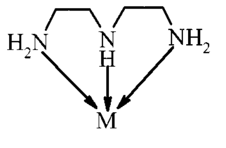
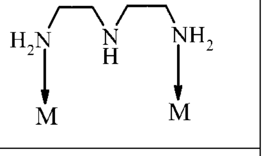
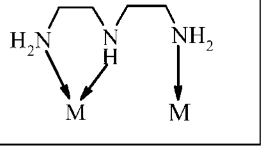
Figure 15. View of the $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]$ molecule in **18**.

Thus, the interaction of $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) cluster anions with Ni^{2+}, Cu^{2+} and Zn^{2+} metal cations in the presence of a chelate ligand such as ethylenediamine leads to the formation of compounds with various structures made up of cluster anions and cationic units corresponding to the different chemical forms that coexist in solutions containing a transition metal salt and en.

4.2. Complexes with Diethylenetriamine

The diethylenetriamine ligand can block one, two or three coordination sites around a transition metal cation. It can also bridge two cations. Table 2 shows the labels of three different coordination modes of the dien molecule.

Table 2. Labels of the coordination modes of the dien molecule.

Labeling	Coordination mode
(1,2,3)-mode	
(1)-(3)-mode	
(1,2)-(3)-mode	

All three coordination modes have been found in complexes containing tetrahedral chalcocyanide rhenium cluster anions and transition metal cations bonded with dien. The (1,2,3)-coordination mode is present in all compounds but the bridging mode only exists in compounds with a dien/M molar ratio greater than 1. A possible reason for this situation is that the K_1 stability constant of $[M(dien)]^{2+}$ (M = Ni, Cu and Zn) is higher than the K_2 constant.

4.2.1. Complexes with Only the (1,2,3)-Coordination Mode

Five complexes containing $\{ML_{n-3}(dien)\}$ cationic units (where L is either ammonia molecules or nitrogen atoms of CN ligands) have been obtained by the reaction of M^{2+} cations (M = Ni, Cu or Zn) with $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) cluster anions in the presence of diethylenetriamine (M/dien = 1:1) in aqueous ammonia solution.

The $[Ni(NH_3)_3(dien)]^{2+}$ chemical form was observed in the ionic compound $[Ni(NH_3)_3(dien)]_2[Re_4Se_4(CN)_{12}]\cdot5.5H_2O$ (**20**), which contains *fac*-$[Ni(NH_3)_3(dien)]^{2+}$ cations (Figure 16). The compound $[\{Ni(NH_3)_2(dien)\}_2Re_4Te_4(CN)_{12}]\cdot2.5H_2O$ (**21**) can be considered the result of an ammonia molecule substitution in a *fac*-$[Ni(NH_3)_3(dien)]^{2+}$ cationic unit by the nitrogen atom of a CN ligand (Figure 17).[28]

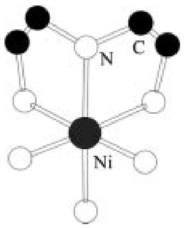


Figure 16. Structure of the complex $[Ni(NH_3)_3(dien)]^{2+}$ cation in compound **20**.

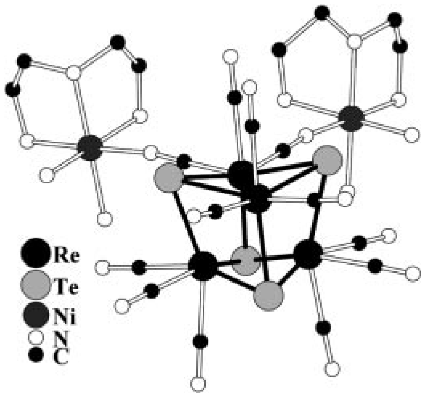


Figure 17. View of the $[\{Ni(NH_3)_2(dien)\}_2Re_4Te_4(CN)_{12}]$ molecule in **21**.

At the same time, the formation of compounds $[\{Cu(NH_3)(dien)\}_2Re_4S_{3.64}Te_{0.36}(CN)_{12}]\cdot3H_2O$ (**22**)[29] and $[\{Cu(NH_3)(dien)\}_2Re_4Se_4(CN)_{12}]\cdot2.5H_2O$ (**23**)[33] can be presented as the result of coordination of a CN ligand to a $[Cu(NH_3)(dien)]^{2+}$ unit with a square-planar structure. The structures of **22** and **23** have only one distinction: in the case of **22** *gem*-CN ligands are bonded to two cationic units, whereas in **23** these bridging ligands have an *ortho* orientation (Figure 18).

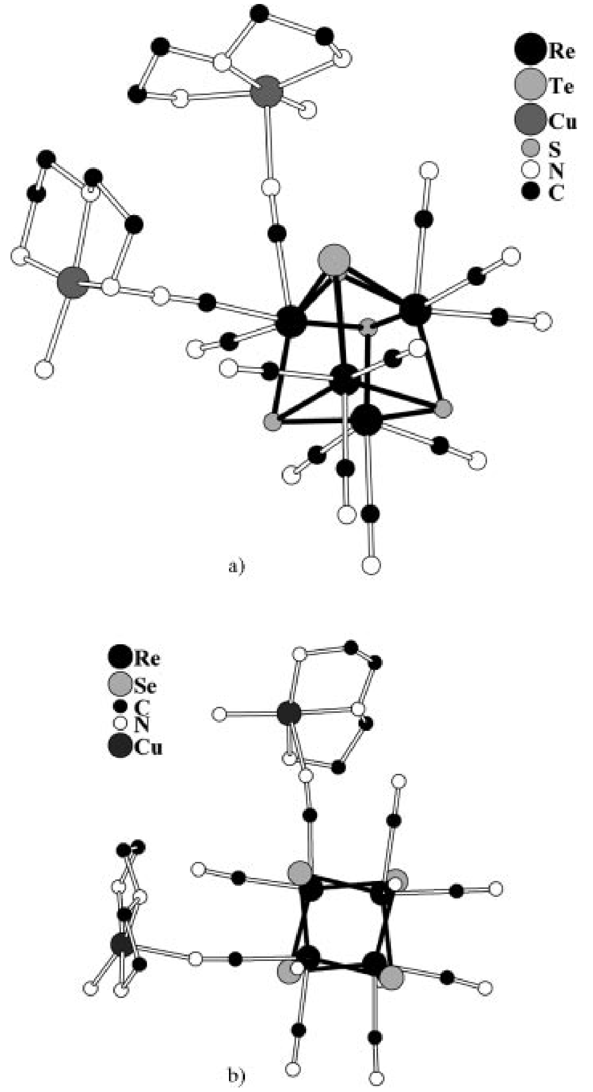


Figure 18. View of the $[\{Cu(dien)(NH_3)\}_2Re_4S_{3.45}Te_{0.55}(CN)_{12}]$ molecule in compound **22** (a) and $[\{Cu(dien)(NH_3)\}_2Re_4Se_4(CN)_{12}]$ molecule in compound **23** (b).

The next step of complication can be viewed in $[\{Cu(dien)\}_2Re_4Te_4(CN)_{12}]\cdot 9H_2O$ (**24**).[27] This compound has a chain-like structure in which the cluster anions are linked to each other through two complex $\{Cu(dien)\}^{2+}$ cations. An alternation of the -2Cu(dien)-cluster-2Cu(dien)-fragments gives rise to a coordination-chain polymer whose structure is shown in Figure 19. Thus, the formation of this compound can be considered as a two-step process. First, the molecular complex $[\{Cu(NH_3)(dien)\}_2Re_4Te_4(CN)_{12}]$, similar to that described for **22**, is formed, and in the next step these molecular units are condensed by means of substitution of an ammonia molecule in the equatorial plane of the copper cation by a nitrogen atom from an adjacent cluster anion.

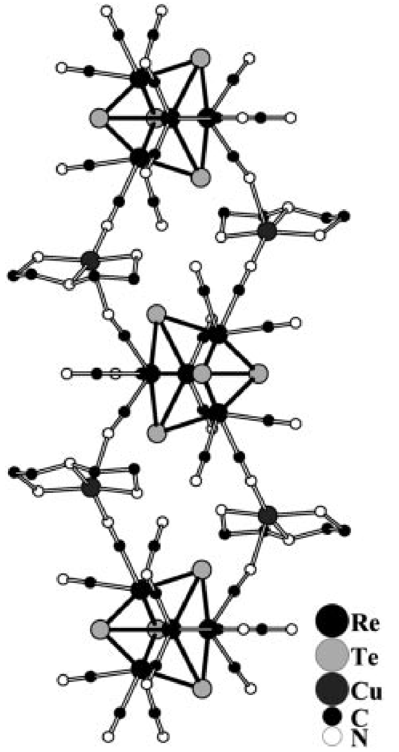


Figure 19. A fragment of the chain in structure of **24**.

We have described above analogous chain structures for compounds **7** and **8** in which the cluster anions are linked to each other by two cationic $\{Cu(NH_3)_3\}^{2+}$ fragments. In the ammonium analog, four CN groups of one cluster anion involved in the formation of the polymeric structure are coordinated to two Re atoms [2 + 2], whereas the bridging CN ligands in the compound with dien are coordinated to three Re atoms [2 + 1 + 1].

4.2.2. A Complex with the (1,3)-Coordination Mode

Decreasing the dien/M^{2+} ratio leads to the formation of complexes in which dien molecules exhibit bridged coordi-

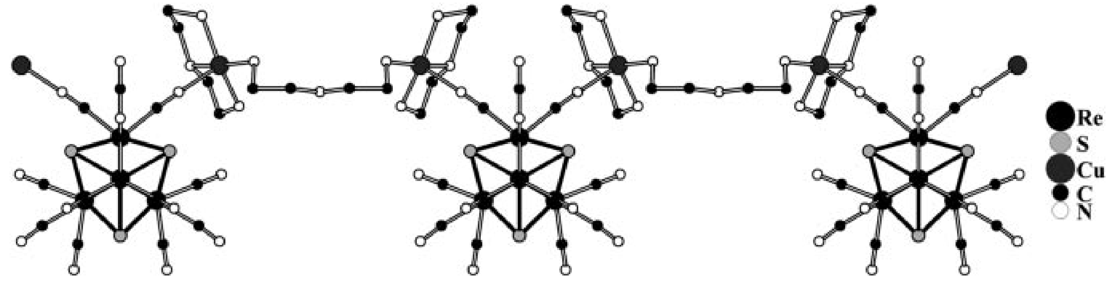


Figure 20. Chain fragment of the structure of compound **25**.

nation modes along with the (1,2,3)-coordination mode. The (1,3)-coordination mode has been found only in the case of $[\{Cu_2(dien)_3\}Re_4S_4(CN)_{12}]$ (**25**),[33] which has a polymeric structure where the $[Re_4S_4(CN)_{12}]^{4-}$ cluster anions are bridged by $[(dien)Cu\text{-}dien\text{-}Cu(dien)]^{4+}$ cationic chains (Figure 20). Each Cu atom in the cationic chain-like building blocks is coordinated by one dien molecule with (1,2,3)-coordination mode and one amino group of bridged dien molecule with (1)-(3)-coordination mode. On the other hand the formation of this compound can be also considered as a result of two-step process. On the first step the formation of $[\{Cu(NH_3)(dien)\}_2Re_4S_4(CN)_{12}]$ takes place analogously to that described for **22**. And then these molecular units are linked by dien molecules which substitute ammonia molecule in equatorial plane of copper cation by terminal amino groups.

4.2.3. The Complexes with (1,2)-(3)-Coordination Mode

The two isostructural compounds $[\{Cu_2(dien)_3\}\text{-}Re_4Q_4(CN)_{12}]\cdot nH_2O$ [Q = Se (**26**) and Te (**27**)] have been synthesised following the same synthetic procedure.[33] It is very interesting to note that both these compounds have a compositions similar to that of **25**, but their structures are sufficiently different. Whereas compound **25** has a chain-like polymeric structure, **26** and **27** are molecular (Figure 21) and consist of $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = Se, Te) cluster anions and non-binding $[Cu_2(dien)_3]^{4+}$ cationic units, the structure of which differs noticeably from the corresponding cation in **25**. Both Cu atoms in **25** are crystallographically equivalent and are coordinated by N atoms of CN ligands of different clusters. In **26** and **27**, however, the Cu atoms exhibit different coordination environments: one Cu atom has a similar arrangement to the Cu atom in compound **25**, whereas the second Cu atom is coordinated by three N atoms of one dien ligand and by two N atoms of another dien ligand, in a (1,2)-(3)-mode, which bridges the two Cu atoms of the cationic unit through its third N atom. Such a coordination type prevents the formation of a polymeric structure. A comparison of **26** and **27** with **25** shows that the structure of the latter can be transformed into the structure of **26** and **27** by the rupture of one Cu–NC bond and the formation of a new bond with the middle amino group of the bridging dien ligand.

The composition of $[\{Zn_2(dien)_3\}Re_4Te_4(CN)_{12}]\cdot 6H_2O$ (**28**)[26] is similar to that of **26** and **27**. However, its molecular structure looks like **26** and **27** only partially. The structure of the $[Zn_2(dien)_3]^{4+}$ cationic unit is analogous to $[Cu_2(dien)_3]^{4+}$ in **26** and **27**, but it is bonded to the cluster cation through not one but two CN ligands, i.e. in this case both metal cations are coordinated by nitrogen atoms of CN ligands (Figure 22). Thus, there are interesting structural transitions between **25** and **26** (or **27**), and then **28**, in which the dimensionality initially decreases from 1D to 0D due to the rupture of an M–NC bond, with an adjustment of the cluster cation and the formation of a new bond inside one molecular unit.

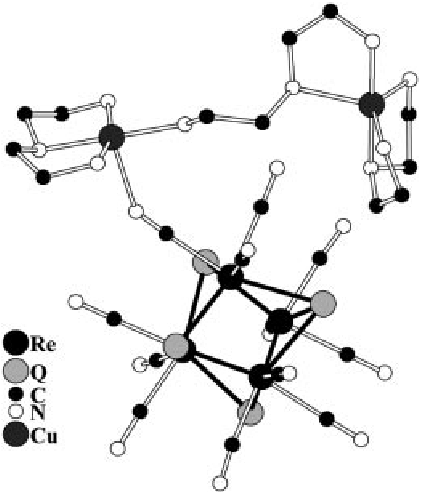


Figure 21. View of the $[\{Cu_2(dien)_3\}Re_4Se_4(CN)_{12}]$ molecule in compound **26** and **27**.

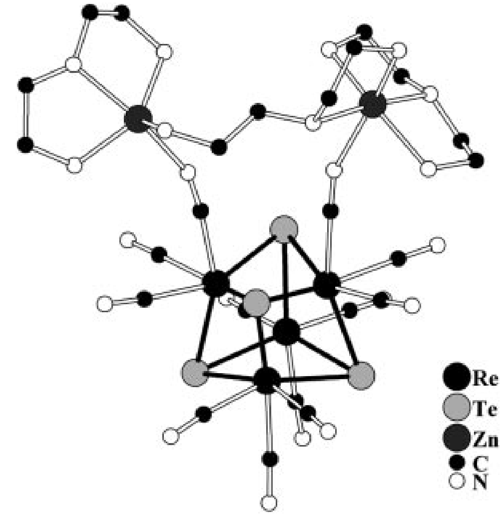


Figure 22. View of the $[\{Zn_2(dien)_3\}Re_4Te_4(CN)_{12}]$ molecule in compound **28**.

If the Cu^{2+} concentration is reduced the isostructural compounds $[K(H_2O)_2]_2[\{Cu_3(dien)_4\}\{Re_4Q_4(CN)_{12}\}_2]\cdot 8H_2O$ [Q = Se (**29**) and Te (**30**)] can be obtained.[33] The anionic unit of this structure is provided by the complex $[\{Cu_3(dien)_4\}\{Re_4Te_4(CN)_{12}\}_2]^{2-}$ (Figure 23), in which two $[Re_4Te_4(CN)_{12}]^{4-}$ cluster anions are bridged by the cation $[Cu_3(dien)_4]^{6+}$, which can be described as [(dien)Cu-(dien)-Cu(dien)-Cu(dien)]. There are two symmetry-equivalent Cu atoms, each coordinated by three N atoms of one dien ligand, one N atom of the bridging dien ligand [(1,2)-(3)-coordination mode], and by one N atom of a CN ligand of the $[Re_4Q_4(CN)_{12}]^{4-}$ anion. The third Cu atom lies at the centre of this cation and is symmetrically coordinated by four N atoms of two bridging dien ligands and at the same time by two additional *trans*-situated N atoms of CN ligands of two different anions (Figure 23). Thus, this Cu atom is octahedrally coordinated and bridges the $[\{Cu_3(dien)_4\}\{Re_4Te_4(CN)_{12}\}_2]^{2-}$ anionic units to construct the polymeric structure. The negative charge of this one-dimensional network is compensated by K^+ cations.

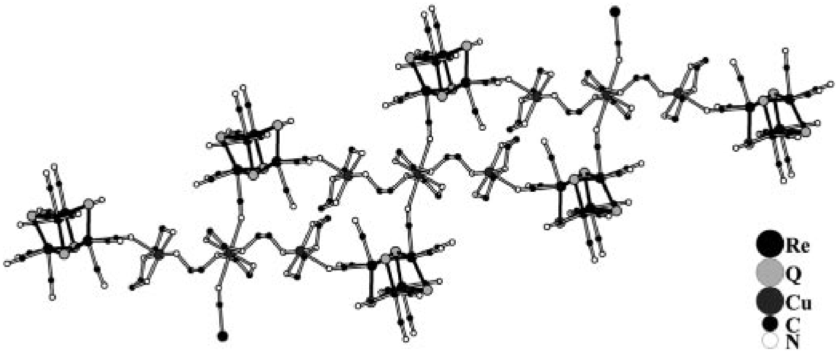


Figure 23. Anionic connectivity pattern in the crystal structure of compounds **29** and **30**.

Thus, the interaction of $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) cluster anions with Ni^{2+}, Cu^{2+}, and Zn^{2+} in the presence of the tridentate ligand diethylenetriamine leads to the formation of a number of complex cluster compounds containing different cationic units: mononuclear $\{M(NH_3)_{n-4}(dien)\}$ or polynuclear $\{M_2(dien)_3\}^{4+}$ and $\{Cu_3(dien)_4\}^{6+}$. The obtained complexes allow us to trace the structural connection between the compounds formed in this system. The parameters affecting the structural type are:

Ratio of reagents: When the M/dien ratio is 1:1 compounds with a (1,2,3)-coordination mode of dien are formed. The M/cluster anion ratio is also important. Although in all these reactions the concentration of M^{2+} ions was sufficient to form complexes containing only M^{2+} cations, two compounds (**29** and **30**) were obtained that crystallise with additional K^+ cations. This may be due to structural factors: these compounds contain longer oligomeric cations $\{Cu_3(dien)_4\}^{6+}$.

The cluster core composition: The influence of this parameter is obvious in the case of **25**, **26**, and **27**, where, on going from Q = S to Q = Se and Te, the structure changes from chain-like to molecular.

The coordination polyhedron of the transition metal cation: The Ni^{2+} cation prefers a rigid octahedral environment, Cu^{2+} a square-pyramidal [4+1] or distorted octahedral [4+2] environment, and Zn^{2+}, with n = 5 or 6, can have various coordination polyhedra.

Compounds **25**–**30** are of particular interest because they contain cations (Cu^{2+}, Zn^{2+}) with bridging coordination modes of the dien molecule. Such coordination modes have not previously been observed in M complexes; in all similar complexes three N atoms of the dien ligand are always coordinated to one M atom as, for example, in $[Cu(dien)]_3[Fe(CN)_6]_2\cdot 6H_2O$.[34] There are only two known examples of metal compounds (both Ag-containing complexes) with bridging dien ligands.[35] Compound **23** is the first example in which the (1,3)-coordination of dien is realized.

4.3. Complexes with Triethylenetetraamine

Complexes have also been obtained with the next member of this homologous series, namely triethylenetetraamine. The interaction of Cu^{2+} with $[Re_4Q_4(CN)_{12}]^{4-}$ (Q_4 = Se_4, Te_4, STe_3) cluster anions in the presence of trien leads to the formation of complexes formulated as $[\{Cu(trien)\}_2Re_4Q_4(CN)_{12}]\cdot nH_2O$ (Q_4 = Se_4 (**31**),[27] Te_4 (**32**),[36] STe_3 (**33**) [32]). *trien* is present in these compounds as a tetradentate ligand occupying four coordination sites. The fifth coordination site is occupied by a nitrogen atom of a bridging CN ligand (Figure 24). In the structures of the compounds, two crystallographically independent $[Cu(trien)]^{2+}$ cations are bonded by the nitrogen atoms of the *meta*-CN ligands of one $[Re_4Q_4(CN)_{12}]^{4-}$ anion. Thus, the formation of these complexes can be considered as a result of coordination of CN groups of the cluster anion to two $[Cu(trien)]^{2+}$ complex cations. It should be noted that this chemical form is the most stable in solution.

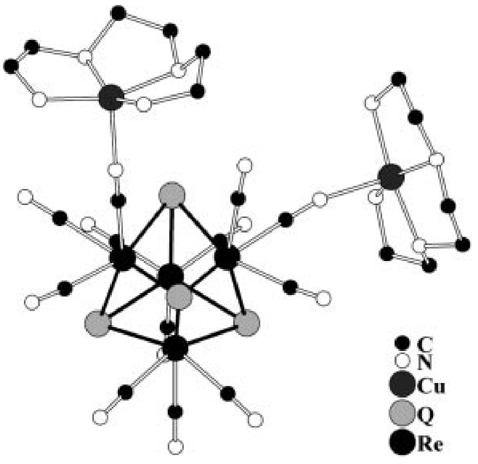


Figure 24. View of the $[\{Cu(trien)\}_2Re_4Q_4(CN)_{12}]$ molecule in compounds **31**–**33**.

Several examples of compounds containing a $[Cu(trien)]^{2+}$ complex cation with a square-pyramidal copper atom, namely [CuL(trien)] compounds (L = SCN^-,[37] NCS^-,[38] I^-,[39] $N(CN)_2^-$,[40]) and also three recently obtained $[Cu(NH_3)(trien)]_2[Re_6Q_8(CN)_6]\cdot nH_2O$ (Q = S, Se, Te)[41] complexes have been described in the literature. In all these cases the coordination environment of the copper atoms is formed by a triethylenetetraamine molecule in the equatorial plane with an L ligand or NH_3 molecule in the apical positions with structures close to those of **31**–**33**.

The reaction of Ni^{2+} with $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se) cluster anions in the presence of trien leads to the formation of $[Ni(NH_3)_2(trien)][\{Ni(NH_3)(trien)\}Re_4Se_4(CN)_{12}]\cdot 2.5H_2O$ (**34**) and $[\{Ni(trien)\}_2Re_4S_4(CN)_{12}]\cdot 3H_2O$ (**35**), which have various crystal structures. The *trien* ligand in these complexes is also tetradentate, occupying four coordination sites in the Ni atom environment; two more coordination sites are occupied either by ammonia molecules or by nitrogen atoms of CN ligands.[28] The $[Ni(NH_3)_2(trien)]^{2+}$ chemical form is observed in **34**. The structure of the $[\{Ni(NH_3)(trien)\}Re_4Se_4(CN)_{12}]^{2-}$ anion (Figure 25) can be viewed as the result of substitution of an ammonia molecule in $[Ni(NH_3)_2(trien)]^{2+}$ by a nitrogen atom of a CN ligand. However, there is a difference in the conformations of the trien ligands in the cationic and anionic complexes. In **35**, the nitrogen atoms of the CN ligands of various cluster anions substitute two ammonia molecules in $[Ni(NH_3)_2(trien)]^{2+}$, binding each other and giving a 1D structure (Figure 26, a). It should be noted that **35** also shows conformational disorder (Figure 26, b and c), the reason for which seems to be the presence of various chemical forms in solution corresponding to different coordination types of triethylenetetraamine.

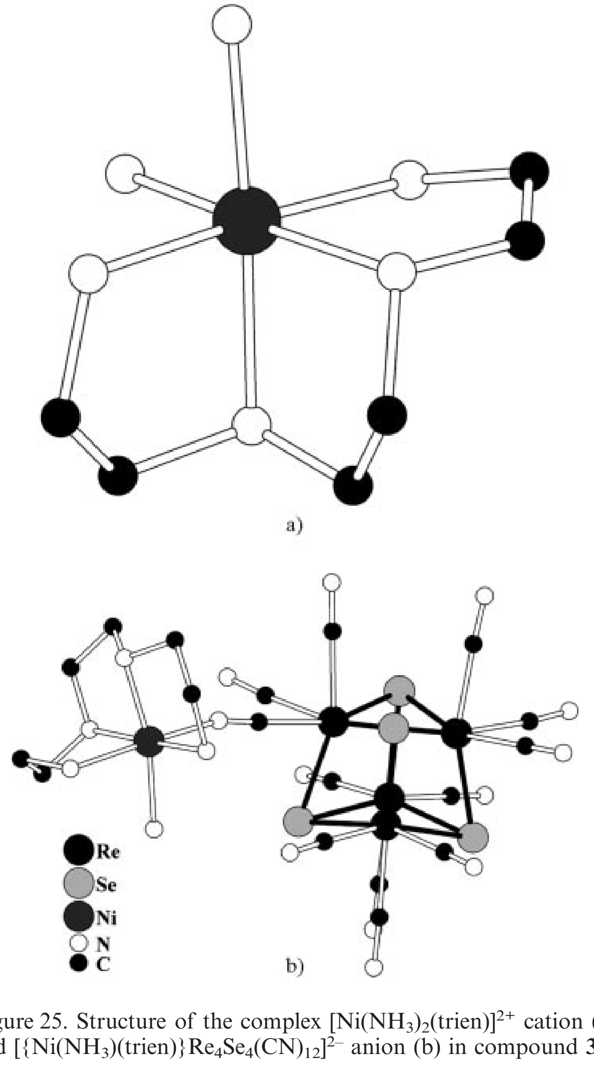


Figure 25. Structure of the complex $[Ni(NH_3)_2(trien)]^{2+}$ cation (a) and $[\{Ni(NH_3)(trien)\}Re_4Se_4(CN)_{12}]^{2-}$ anion (b) in compound **34**.

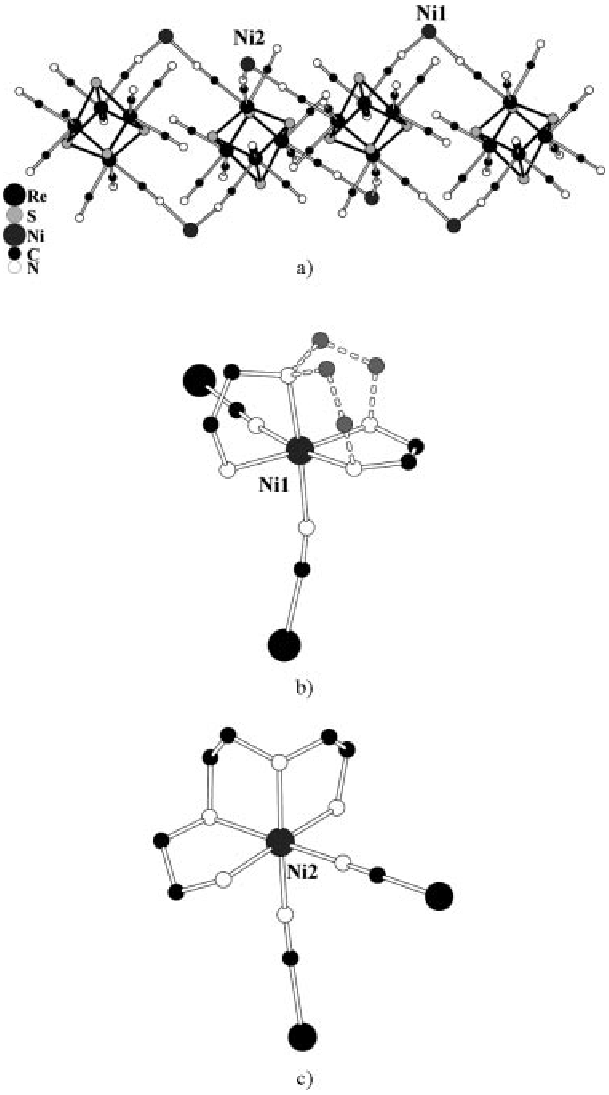


Figure 26. a) A fragment of the structure of **35**; trien ligands have been omitted for clarity. b) The coordination environment of the Ni1 cations. c) The coordination environment of the Ni2 cations.

The chain-like structure of **35** is similar to that of **24**. Based on these two compounds, the connection between ligand denticity, the coordination number of the metal cation, and the formation of a certain structural type can be traced easily. In **24**, the dien molecule occupies three coordination sites in the copper atom environment such that the copper atoms have $n = 5$. Correspondingly, there are two coordination sites open for bonding to CN ligands. An analogous situation is observed in **35** with only one difference: the trien molecule occupies four coordination sites in the environment of nickel atoms with $n = 6$.

4.4. Complexes with *threo*-Tetraaminobutane

(1,2*S*,3*S*,4)-Tetraaminobutane, like triethylenetetraamine, has four amino groups, however, this ligand coordinates preferably in a bis-didentate mode with a metal–metal separation of about 7 Å. The bis-didentate coordination mode arises from steric constraints, which prevent binding of the four amino donor atoms to the same metal centre. As has been shown previously,[42] this results in the formation of chiral {...(*threo*-tab)-Cu-(*threo*-tab)...}$_n$ oligomeric species with a linear chain structure and square-planar {CuN_4} units. Additional binding of a bridging unit to the axial positions of the Cu^{2+} centres would thus provide a route to new, two-dimensional and chiral metal organic frameworks with an open structure. The bridging unit would serve as a spacer, and its size and structure could be used to adjust the distance between individual {[Cu(*threo*-tab)]$^{2+}$}$_\infty$ strands.

This strategy has been exploited by using $[Re_4Q_4(CN)_{12}]^{4-}$ clusters as bridging units to interlink linear [{Cu(*threo*-tab)}$^{2+}$]$_\infty$ strands. The crystalline solids [{Cu(*threo*-tab)}$_2Re_4Te_4(CN)_{12}$]·6.5H_2O (**36**) and [{$Cu_2(NH_3)$(*threo*-tab)$_2$}$Re_4Te_4(CN)_{12}$]·4H_2O (**37**) were prepared by direct combination of *threo*-tab, Cu^{2+}, and the rhenium cluster anion in aqueous ammonia solution.[43,44]

There is a clear influence of the individual steric properties of the bridging units possessing different compositions on the grid structure. In the $[Re_4Te_4(CN)_{12}]^{4-}$ ion, for example, the high number of cyano ligands enables different types of Cu-cluster-Cu interactions, and two of them are realized in **36** and **37**. The nitrogen atoms of four CN ligands of the cluster anion take part in binding in compound **36**, and this mode of binding means that all copper atoms are coordinated by CN ligands; at the same time, all copper atoms are equal and have a distorted octahedral [4+2] environment formed by nitrogen atoms (Figure 27).

In compound **37**, two of the twelve CN groups of the cluster anions take part in binding. In this case, only every second copper atom is coordinated by a CN ligand; the remaining copper atoms are coordinated by ammonia molecules. Half of the copper atoms are in a [4+2] environment and the others are in a [4+1] environment. The one-dimensional {...*threo*-tab-Cu-*threo*-tab-Cu-*threo*-tab...}$_\infty$ strands formed by Cu^{2+} cations and *threo*-tab molecules have a complicated zigzag structure (Figure 28).

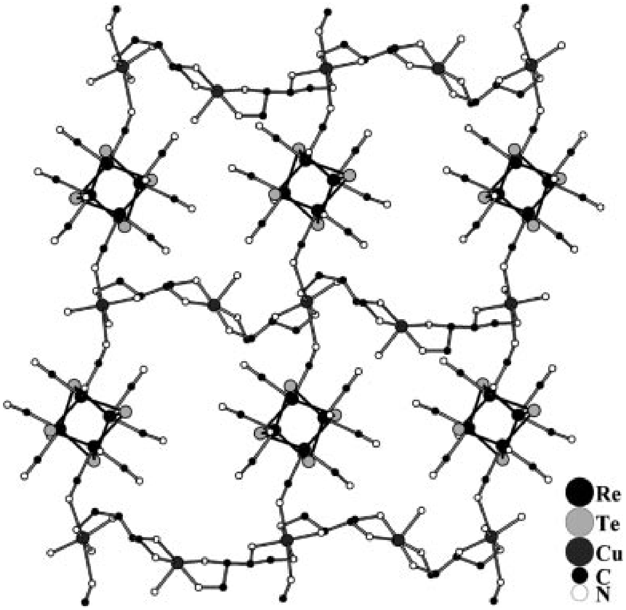


Figure 28. A fragment of the [{$Cu_2(NH_3)$(*threo*-tab)$_2$}$Re_4Te_4(CN)_{12}$] polymer layer in **37**.

The third type of packing is realized in the compound [{$Cu(NH_3)$(*threo*-tab)}]$_2$[$Re_4S_{3.4}Te_{0.6}(CN)_{12}$]·1.25$H_2O$ (**38**),[44] which contains undulating, infinite {...*threo*-tab-Cu-*threo*-tab...}$_\infty$ chains that are weakly bonded to cluster anions. The nearest Cu–N(CN ligand) distance is 2.95 Å. In this case, the cluster anions are situated in voids formed by chain packing. The Cu^{2+} cations have a typical five-coordinate environment with four nitrogen atoms from *threo*-tab and an ammonia molecule (Figure 29).

The question as to what caused the structures to be so different in these systems was answered when it was found that in the case of tetrahedral rhenium complexes the structure of the formed coordination polymer depends on two factors, namely the method of synthesis and the cluster core structure.[44]

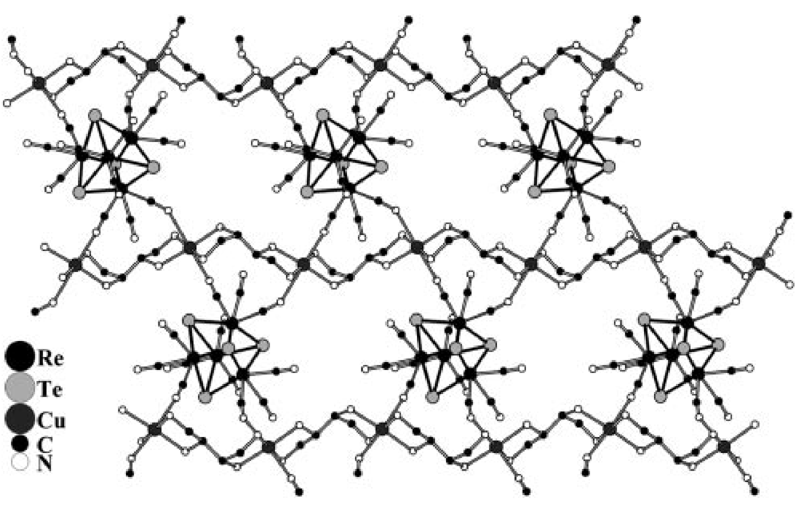


Figure 27. A fragment of the [{Cu(*threo*-tab)}$_2Re_4Te_4(CN)_{12}$] polymer layer in **36**.

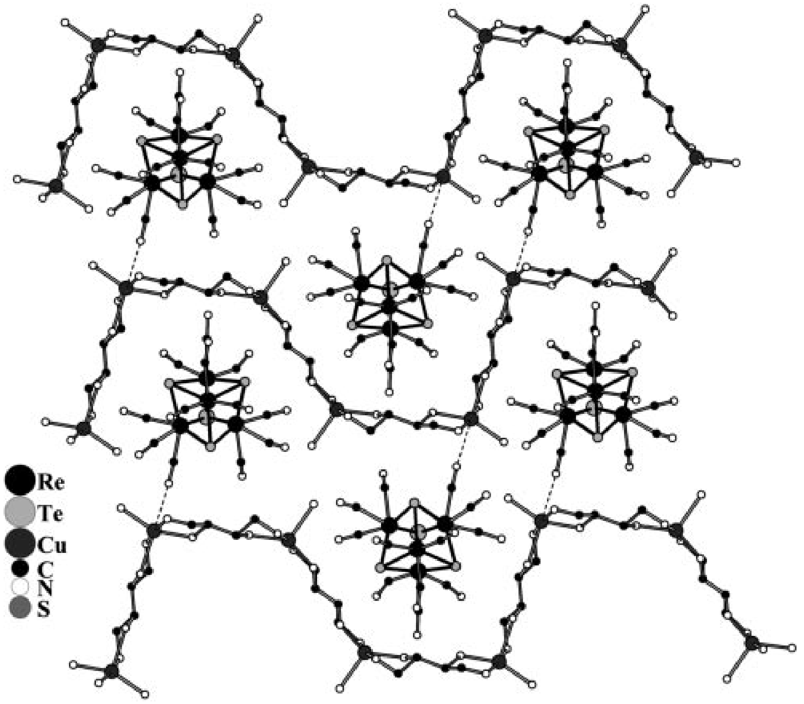


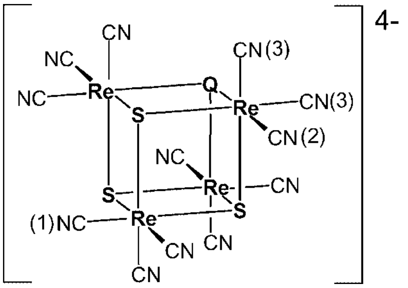
Figure 29. Mutual arrangement of {...(*threo*-tab)-Cu-(*threo*-tab)-Cu-(*threo*-tab)...} chains and location of the cluster anions in **38** (the shortest distances between the N atoms of the CN groups in the cluster anions and the Cu atoms in the polymer chains are shown as dashed lines).

4.5. Complexes Containing $Re_4S_{4-x}Te_x$ Cluster Cores

According to the single crystal diffraction analyses, compounds **14**, **16**, **19**, **22**, **33** and **38** contain mixed S/Te chalcogenide ligands in the cluster core $\{Re_4S_{4-x}Te_x\}$. The starting cluster compound $K_4[Re_4S_{4-x}Te_x(CN)_{12}]$ has been synthesised accidentally during preparation of the cluster $K_4[Re_4S_4(CN)_{12}]$ from $[Re_4S_4(TeCl_2)_4Cl_8]$ by boiling with KCN as described for $K_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$.[11] According to elemental analysis, the compound obtained contains tellurium. This could be due to a sulfur shortage during the preparation of $[Re_4S_4(TeCl_2)_4Cl_8]$ from $ReCl_5$, S and Te.[10]

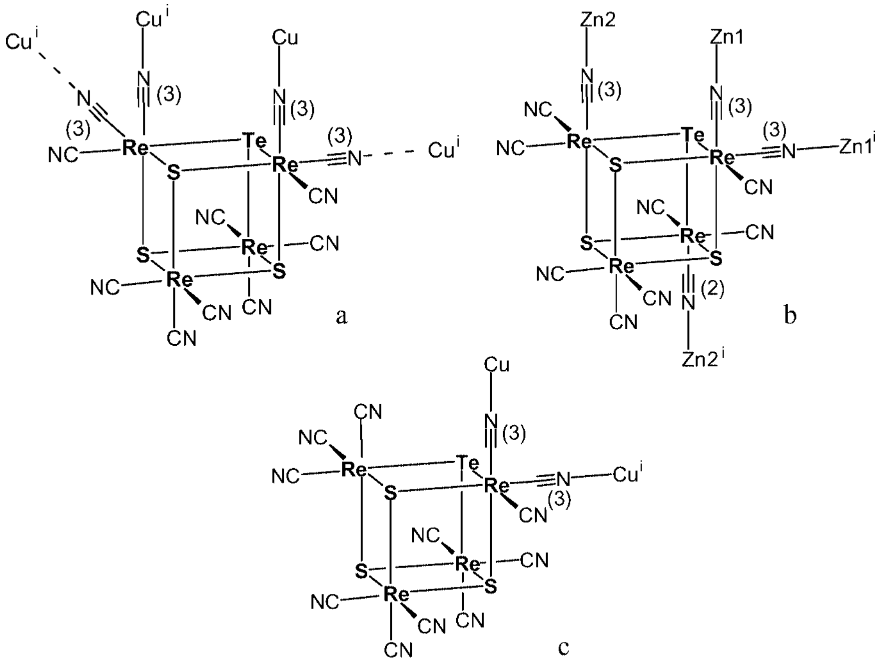
In compounds **14**, **16** and **22** there are two different cluster anions, with compositions $[Re_4S_4(CN)_{12}]^{4-}$ and $[Re_4S_3Te(CN)_{12}]^{4-}$. In the latter cluster one sulfur atom is substituted by a tellurium atom. In the structures of all three compounds the Re_4S_4 and Re_4S_3Te cluster cores are ordered in such a way that three positions of the Q_4 tetrahedron are equivalent and occupied by only sulfur atoms; the fourth position is occupied by either a sulfur or a tellurium atom.

It should be noted that in all three structures the metal cations are bound to the CN groups that are closest to the tellurium atom position. To understand the reason for this density functional theory calculations have been carried out on different $[Re_4S_3Q(CN)_{12}]^{4-}$ (Q = S, Se, Te) cluster anions with the ADF program.[45] According to these calculations, there are several types of CN ligands in these cluster anions. Considering each Re atom to be octahedrally coordinated, without taking Re–Re bonds into account (Scheme 2), there are three CN groups bonded to the ReS_3 fragment (type 1). The remaining CN ligands are coordinated to three ReS_2Q (Q = Se, Te) fragments. Within the $ReS_2Q(CN)_3$ units, one CN group is more distant from the Q atom than the other two groups (these ligands are denoted types 2 and 3, respectively). For CN ligands of types 1 and 2 the changes are negligible, but for six CN groups of the third type they are considerable and increase with a decrease of the electronegativity of the chalcogen atoms. The increase of negative charge on the N atoms of type 3 results in a considerable preference for the metal ions to coordinate to these atoms.



Scheme 2.

All copper atoms in compound **14** are coordinated by CN groups of type 3 to give a polymeric structure (Scheme 3, a). This differs slightly from compound **16**, in which the Zn1 atoms are coordinated by two CN groups of type 3 whereas the Zn2 cations are linked to CN groups of both types 2 and 3. To put it another way, only three of the four bridging CN ligands of one cluster anion are of type 3, while the fourth one is of type 2 (Scheme 3, b). In molecular



Scheme 3.

compound **22**, two bridging CN groups also belong to type 3 (Scheme 3, c).

It was also interesting to study the behaviour of the {Re_4STe_3} cluster core in similar systems. For this, the cluster salt $K_4[Re_4STe_3(CN)_{12}]\cdot 5H_2O$ (**I**) was synthesised and characterised.[32] However, in compounds **19** and **33** the expected ordering of sulfur positions was not observed. The sulfur atoms are disordered over two (**19**) or four (**33**) of the apexes of the tetrahedron. One of the possible reasons for this might be the cluster core composition of the starting materials, which could contain {$Re_4S_2Te_2$} and {Re_4Te_4} clusters as well as {Re_4STe_3}.

5. Conclusions

Throughout this microreview we have mainly reported the isolation and characterisation of various complexes based on tetranuclear rhenium cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) and transition metal cations, the coordination sites of which are fully or partially occupied by water molecules or N-donor ligands, particularly ammonia, ethylenediamine, diethylenetriamine, triethylenetetraamine and chiral *threo*-tetraaminobutane. The structures of all compounds have been confirmed by single-crystal X-ray analysis.

We should emphasise, again, that the composition and structure of the obtained compounds are determined by several parameters, namely:

1) the reagent ratio: M^{2+} cation/polydentate ligand or M^{2+} cation/cluster anion;
2) the M^{2+} cation coordination environment;
3) the coordination number and coordination polyhedron of the M^{2+} cations;
4) the cluster core composition.

It has been shown that the reaction of chalcocyanide rhenium cluster complexes $[Re_4Q_4(CN)_{12}]^{4-}$ with cations of 3d-transition metals (Ni^{2+}, Cu^{2+}, Zn^{2+}) in the presence of chelating ligands gives many complex compounds with various structures (ionic, molecular or polymeric). Complicated cluster complexes with polymeric structures containing bridging polydentate ligands, namely diethylenetriamine and *threo*-tetraaminobutane, were obtained for the first time.

We have also introduced a new and straightforward synthetic pathway to heterometallic and chiral coordination polymers. The use of oligonuclear bridging units has proved to be of particular interest because it allows the design of open networks with sufficiently large voids for host–guest interactions. More importantly, the use of the chiral, bisdidentate *threo*-tab ligand guarantees the formation of a chiral crystal structure which has the ideal prerequisites for the coating of suitable surfaces with a chiral monolayer.

Complexes containing mixed-ligand {$Re_4S_{4-x}Te_x$} cluster cores have been obtained and characterised for the first time. Their structural data supplement previous research and show that six CN groups of the cluster anion can be activated for interaction with metal cations by substituting one sulfur atom by a tellurium atom in the Re_4S_4 cluster core; these groups are those nearest to the Te atom.

Acknowledgments

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[1] Y. V. Mironov, V. E. Fedorov, *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 569–580.

[2] I. V. Kalinina, V. P. Fedin, *Russ. J. Coord. Chem.* **2003**, *29*, 597–615.
[3] S. Harris, *Polyhedron* **1989**, *8*, 2843–2882.
[4] T. Saito, *J. Chem. Soc., Dalton Trans.* **1999**, 97–105.
[5] Y. V. Mironov, E. Albrecht-Schmitt, J. A. Ibers, *Inorg. Chem.* **1997**, *36*, 944–946.
[6] E. S. Lang, U. Abram, J. Strähle, *Z. Anorg. Allg. Chem.* **1996**, *622*, 251–253.
[7] Y. V. Mironov, S. S. Yarovoi, D. Y. Naumov, N. V. Kuratieva, S. V. Kozlova, A. Simon, V. E. Fedorov, *Eur. J. Inorg. Chem.* **2005**, 2476–2479.
[8] Y. V. Mironov, M. A. Pell, T. E. Albrecht-Schmitt, J. A. Ibers, *Inorg. Chem.* **2001**, *40*, 5472–5474.
[9] Y. V. Mironov, *Polyhedron* **2000**, *19*, 437–439.
[10] Y. V. Mironov, T. E. Albrecht-Schmitt, J. A. Ibers, *Z. Kristallogr.* **1997**, *212*, 308.
[11] Y. V. Mironov, A. V. Virovets, W. S. Sheldrick, V. E. Fedorov, *Polyhedron* **2001**, *20*, 969–974.
[12] Y. V. Mironov, *Eur. J. Inorg. Chem.* **1999**, 997–999.
[13] N. G. Naumov, A. V. Virovets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem. Int. Ed.* **1998**, *37*, 1943–1945.
[14] L. G. Beauvais, M. P. Shores, J. R. Long, *Chem. Mater.* **1998**, *10*, 3783–3786.
[15] M. V. Bennett, L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2001**, *123*, 8022–8032.
[16] Y. Kim, S.-M. Park, W. Nam, S.-J. Kim, *Chem. Commun.* **2001**, 1470–1471.
[17] S. B. Artemkina, N. G. Naumov, A. V. Virovets, V. E. Fedorov, *Eur. J. Inorg. Chem.* **2005**, 142–146.
[18] M. S. Tarasenko, A. Y. Ledneva, N. G. Naumov, D. Y. Naumov, V. E. Fedorov, *J. Cluster Sci.* **2005**, *16*, 353–365.
[19] N. G. Naumov, M. S. Tarasenko, A. V. Virovets, Y. Kim, S. J. Kim, V. E. Fedorov, *Eur. J. Inorg. Chem.* **2006**, 298–303.
[20] S. Jin, F. J. DiSalvo, *Chem. Mater.* **2002**, *14*, 3448–3457.
[21] B. B. Yan, H. J. Zhou, A. Lachgar, *Inorg. Chem.* **2003**, *42*, 8818–8822.
[22] Z. H. Yan, C. S. Day, A. Lachgar, *Inorg. Chem.* **2005**, *44*, 4499–4505.
[23] Y. V. Mironov, A. V. Virovets, S. B. Artemkina, V. E. Fedorov, *Angew. Chem. Int. Ed.* **1998**, *37*, 2507–2509.
[24] Y. V. Mironov, O. Oeckler, A. Simon, V. E. Fedorov, *Eur. J. Inorg. Chem.* **2001**, 2751–2753.
[25] Y. V. Mironov, O. A. Efremova, V. E. Fedorov, O. Oecler, A. Simon, C. Vicent, R. Lusar, *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 1698–1701.
[26] Y. V. Mironov, O. A. Efremova, D. Y. Naumov, V. E. Fedorov, *Russ. Chem. Bull. Int. Ed.* in press.
[27] Y. V. Mironov, O. A. Efremova, S. F. Solodovnikov, N. G. Naumov, W. S. Sheldrick, A. Perrin, V. E. Fedorov, *Russ. Chem. Bull. Int. Ed.* **2004**, *53*, 2129–2134.
[28] O. A. Efremova, Y. V. Mironov, N. V. Kuratieva, V. E. Fedorov, *Russ. J. Coord. Chem*. in press.
[29] O. A. Efremova, Y. V. Mironov, D. Y. Naumov, S. G. Kozlova, V. E. Fedorov, *Polyhedron* **2006**, *25*, 1233–1238.
[30] K. A. Brylev, Y. V. Mironov, N. G. Naumov, V. E. Fedorov, J. A. Ibers, *Inorg. Chem.* **2004**, *43*, 4833–4838.
[31] Y. V. Mironov, V. E. Fedorov, I. Ijjaali, J. A. Ibers, *Inorg. Chem.* **2001**, *40*, 6320–6323.
[32] O. A. Efremova, Y. V. Mironov, D. Y. Naumov, V. E. Fedorov, *J. Struct. Chem*. in press.
[33] Y. V. Mironov, O. A. Efremova, D. Y. Naumov, W. S. Sheldrick, V. E. Fedorov, *Eur. J. Inorg. Chem.* **2003**, 2591–2595.
[34] H.-Z. Kou, D.-Z. Liao, P. Cheng, Z.-H. Jiang, S.-P. Yan, G.-L. Wang, X.-K. Yao, H.-G. Wang, *J. Chem. Soc., Dalton Trans.* **1997**, 1503–1506.
[35] E. C. Plappert, D. M. P. Mingos, S. E. Lawrence, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **1997**, 2119–2123.
[36] O. A. Efremova, Y. V. Mironov, D. Y. Naumov, V. E. Fedorov, *J. Struct. Chem.* **2005**, *46*, 973–977 (in Russian).
[37] G. Marongiu, E. C. Lingafelter, P. Paoletti, *Inorg. Chem.* **1969**, *8*, 2763–2767.
[38] G. Marongiu, M. Gannas, *J. Chem. Soc., Dalton Trans.* **1979**, 41–44.
[39] V. Manriquez, M. Campos Vallette, N. Lara, N. Gonzalez Tejeda, O. Wittke, G. Diaz, S. Diaz, R. Munoz, L. Kriskovic, *J. Chem. Crystallogr.* **1996**, *26*, 15–22.
[40] J. Luo, X. G. Zhou, L. H. Weng, X. F. Hou, *Acta Crystallogr. Sect. C* **2003**, *59*, m392–m395.
[41] K. A. Brylev, N. G. Naumov, G. Peris, R. Lusar, V. E. Fedorov, *Polyhedron* **2003**, *22*, 3383–3387.
[42] A. Zimmer, D. Kuppert, T. Weihermüller, I. Müller, K. Hegetschweiler, *Chem. Eur. J.* **2001**, *7*, 917–931.
[43] Y. V. Mironov, N. G. Naumov, K. A. Brylev, O. A. Efremova, V. E. Fedorov, K. Hegetschweiler, *Angew. Chem. Int. Ed.* **2004**, *43*, 1297–1300.
[44] Y. V. Mironov, N. G. Naumov, K. A. Brylev, O. A. Efremova, V. E. Fedorov, K. Hegetschweiler, *Russ. J. Coord. Chem.* **2005**, *31*, 269–281.
[45] Amsterdam Density Functional (ADF) program, release 2002.02; Vrije Universteit, Amsterdam, The Netherlands, **2002**.

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