Structural Diversity of Low-Dimensional Compounds in $[M(en)_2]^{2+}/[Re_6Q_8(CN)_6]^{4-}$ Systems (M = Mn, Ni, Cu)

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Five new octahedral chalcocyanide cluster compounds $[\{Mn(H_2O)(en)_2\}\{Mn(en)_2\}Re_6Te_8(CN)_6]\cdot 3H_2O$ (**1**), $[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Se_8(CN)_6]Cl_2\cdot 2H_2O$ (**2**), $[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Te_8(CN)_6]Cl_2\cdot H_2O$ (**3**), $(NH_4)_2[\{Ni(en)_2\}_3\{Re_6Te_8(CN)_6\}_2]\cdot 6H_2O$ (**4**) and $(Et_4N)_2[Cu(NH_3)(en)_2]_2[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]\cdot 2H_2O$ (**5**) (en = ethylenediamine), have been synthesised. All five compounds have been characterised by single-crystal X-ray diffraction analysis. Compounds **1–3** have chain-like polymeric structures, whereas compound **4** exhibits a two-dimensional polymeric structure, with negatively charged $[\{Ni(en)_2\}_3\{Re_6Te_8(CN)_6\}_2]^{2-}_{\infty\infty}$ layers, and compound **5** has an ionic structure where anionic $[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]^{6-}$ dimers are packed with cationic $[Cu(NH_3)(en)_2]^{2+}$ complexes and Et_4N^+ cations.
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Introduction

The coordination chemistry of octahedral rhenium chalcocyanide cluster complexes $[Re_6Q_8(CN)_6]^{4-/3-}$ (Q = S, Se, Te) is in a stage of a rapid development.[1−5] The interaction of these anions with aqua cations of different metals $[M(H_2O)_6]^{n+}$ results in a partial or total replacement of the coordinated water molecules by nitrogen atoms of the more nucleophilic CN ligands. As a rule such interactions lead to three-dimensional polymeric structures where four or all six CN ligands of the cluster anions coordinate to cations through Re−CN−M bridges.[6−12] The number of low-dimensional structures is limited.[13,14]

A set of chain structures and structures with isolated $[\{M(H_2O)_5\}Re_6Q_8(CN)_6]^{2-}$ fragments has been obtained by using large organic cations like Pr_4N^+ or Bu_4N^+ as "spacers" to separate low-dimensional fragments, thus preventing the formation of framework or layered arrays.[15−17] Another approach to obtain low-dimensional structures is to restrict the coordination abilities of the transition metals. This method has been widely used for mononuclear cyanides.[18−26] Recently, this approach has also been applied to octahedral rhenium chalcocyanide cluster anions such as $[Re_6Q_8(CN)_6]^{4-}$. Several types of organic chelate ligands like en (ethylenediamine),[27,28] trien (triethylenetetramine),[29] salen [*N,N'*-ethylenebis(salicylideneaminato)],[30,31] OEP (octaethylporphyrinato dianion) and TPP (tetraphenylporphyrinato dianion)[32] were used and it was shown that the coordination of chelating ligands to the metal effectively reduces the dimensionality of the network.

In the present work we continue the study of the interaction of $[Re_6Q_8(CN)_6]^{4-}$ anions with transition metal cations in the presence of the simplest chelating ligand — ethylenediamine. Five new compounds $[\{Mn(H_2O)(en)_2\}\{Mn(en)_2\}Re_6Te_8(CN)_6]\cdot 3H_2O$ (**1**), $[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Se_8(CN)_6]Cl_2\cdot 2H_2O$ (**2**), $[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Te_8(CN)_6]Cl_2\cdot H_2O$ (**3**), $(NH_4)_2[\{Ni(en)_2\}_3\{Re_6Te_8(CN)_6\}_2]\cdot 6H_2O$ (**4**) and $(Et_4N)_2[Cu(NH_3)(en)_2]_2[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]\cdot 2H_2O$ (**5**) have been prepared and characterised by X-ray diffraction analysis. They demonstrate the structural diversity of compounds formed in the system "$[M(en)_2]^{2+}$ + $[Re_6Q_8(CN)_6]^{4-}$", where M^{2+} is Mn^{2+}, Ni^{2+} or Cu^{2+} and Q is Se or Te.

Results and Discussion

The crystals of compound **1−3** were obtained by diffusion of a water solution of $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ (**1**) or aqueous ammonia solutions of $K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$ (**2**) or $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ (**3**) into the glycerol solutions of $Mn(OAc)_2\cdot 4H_2O$ (**1**) or $NiCl_2\cdot 6H_2O$ (**2** and **3**) in the presence of ethylenediamine. Compounds **4** and **5** were crystallised by mixing of aqueous ammonia solutions of $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ and $NiCl_2\cdot 6H_2O$ or $CuCl_2\cdot 2H_2O$, respectively, in the presence of ethylenediamine [Bu_4NBr (**4**) or Et_4NBr (**5**) were added to the reacting systems].

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In compounds **1**−**5** the structure of the $[Re_6Q_8(CN)_6]^{4-}$ (Q = Se, Te) anions is similar to that in the starting compounds and related complexes.[2−11,14,16,17,27−32] The Re_6 cluster is an almost ideal octahedron, and the Re−Re bond lengths vary from 2.6714(8) to 2.6988(9) Å in **1**, from 2.6270(7) to 2.6330(3) Å in **2**, 2.6828(7) to 2.6880(6) Å in **3**, from 2.677(2) to 2.698(2) Å in **4** and from 2.6862(8) to 2.6937(8) Å in **5**. The chalcogen atoms cap each triangular face of the Re_6 octahedron. The Re−Q bonds range from 2.683(1) to 2.714(1) Å in **1**, from 2.5247(8) to 2.5275(8) Å in **2**, from 2.6927(5) to 2.6984(6) Å in **3**, from 2.688(2) to 2.701(3) Å in **4** and from 2.679(1) to 2.717(1) Å in **5**. Six cyanide ligands coordinate to rhenium atoms through carbon and stick out in pairs in a mutually perpendicular fashion. The Re−C distances range from 2.07(2) to 2.11(2) Å in **1**, from 2.08(1) to 2.104(9) Å in **2**, from 2.063(14) to 2.085(9) Å in **3**, from 2.03(3) to 2.18(3) Å in **4** and from 2.07(1) to 2.11(2) Å in **5**; the C−N distances range from 1.12(2) to 1.17(3) Å in **1**, from 1.15(1) to 1.16(2) Å in **2**, from 1.16(1) to 1.17(2) Å in **3**, from 1.10(4) to 1.22(4) Å in **4** and from 1.14(2) to 1.20(2) Å in **5**.

In the structure of **1** there are two crystallographically independent manganese cations. Each manganese atom is coordinated by two ethylenediamine molecules, which lie in the equatorial plane and occupy four coordination sites, with Mn−N distances ranging from 2.24(3) to 2.32(2) Å. The atoms coordinated in the axial positions differ for each Mn centre: Mn1 is coordinated by the nitrogen atom of a CN group of the cluster anion [Mn−N distance is 2.26(2) Å] and a water molecule, with an Mn−O length of 2.20(1) Å (Figure 1a), whereas the axial coordination sites of Mn2 (Figure 1b) are coordinated by two nitrogens of CN ligands from neighbouring cluster anions, with Mn−N(CN) distances of 2.23(1) Å and 2.25(2) Å, to form a polymeric zig-zag chain of composition $[\{Mn(H_2O)(en)_2\}\{Mn(en)_2\}Re_6Te_8(CN)_6]_\infty$ (Figure 2). The chains are neutral and are connected to each other by hydrogen bonds to solvate water molecules.

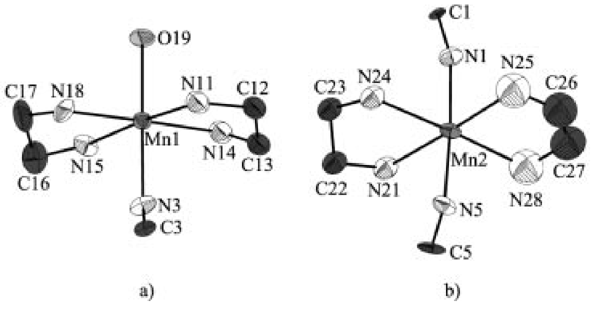

Figure 1. Ligand environment of Mn1 (a) and Mn2 (b) in **1**; displacement ellipsoids are drawn at the 30% probability level; all hydrogen atoms have been omitted for clarity

Compounds **2** and **3** are isostructural. In these compounds there are two crystallographically independent nickel cations. The Ni2 atom and the $[Re_6Q_8(CN)_6]$ clusters have crystallographically imposed *mmm* symmetry, while Ni1 and the Cl atoms have crystallographically imposed 2/*m* and 2*mm* symmetry, respectively. Ni2 is *trans*-coordinated by two nitrogen atoms of CN ligands from neighbouring cluster anions, with Ni2−N(CN) distances of 2.10(1) Å in **2** and 2.06(1) Å in **3**; the four remaining coordination sites are occupied by four molecules of ammonia, with $Ni2-N(NH_3)$ distances of 2.12(2) Å in both compounds (Figure 3a). The Re−CN−Ni2−NC−Re interactions extend along the *a* axis to give infinite negatively charged linear $\{\cdots N{\equiv}C-[Re_6Q_8(CN)_4]-C{\equiv}N-Ni2-N{\equiv}C-[Re_6Q_8(CN)_4]-C{\equiv}N\cdots\}_\infty$ chains (Figure 4a). Ni1 forms the cationic complex *trans*-$[Ni(NH_3)_2(en)_2]^{2+}$ (Figure 3b). The $Ni1-N(NH_3)$ distances are 2.183(8) Å in **2** and 2.187(8) Å in **3**, and the Ni1−N(en) distances are 2.109(6) Å in **2** and 2.108(6) Å in **3**. The structure also contains Cl^- anions surrounded by two $[Ni(NH_3)_2(en)_2]^{2+}$ complex cations [shortest Cl−N(en) distances are 3.41 Å in **2** and 3.47 Å in **3**]. The water molecules are situated near these Cl atoms. The shortest Cl−O distances are 3.15 Å in **2** and 3.27 Å in **3** and correspond to relatively strong Cl···H−O hydrogen bonds.

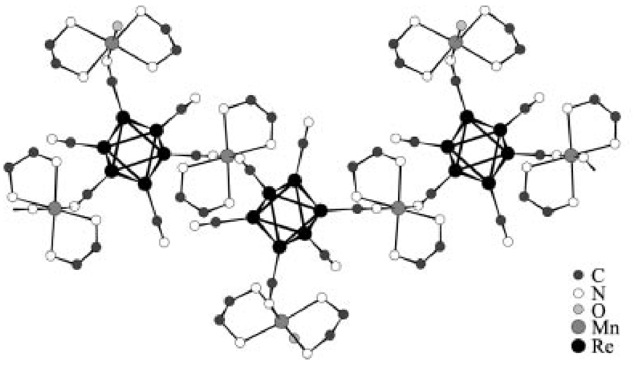

Figure 2. Fragment of the polymer chain $[\{Mn(H_2O)(en)_2\}\{Mn(en)_2\}Re_6Te_8(CN)_6]_\infty$; all hydrogen and tellurium atoms have been omitted for clarity

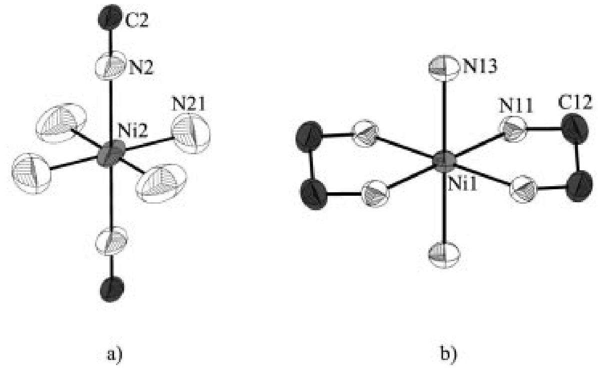

Figure 3. Ligand environment of Ni2 (a) and Ni1 (b) in **2** and **3** (only **2** is shown); displacement ellipsoids are drawn at the 50% probability level; all hydrogen atoms have been omitted for clarity

Infinite anionic chains are located in the same plane and are shifted relative to each other by half a unit cell translation along the *a* axis, as shown in Figure 4b. The distances between chains lying in adjacent planes are 11.822(5) Å in **2** and 12.1078(3) Å in **3**, and 8.078(3) Å in **2** and 8.2025(2) Å in **3** between chains lying in the same plane;

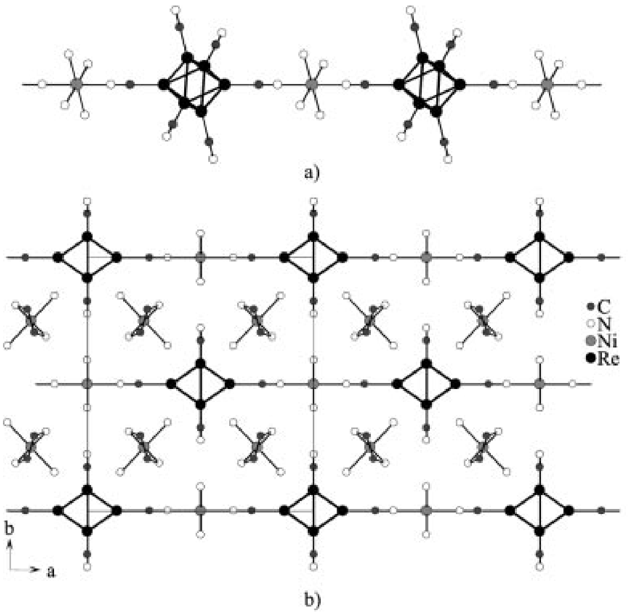

Figure 4. A fragment of the negatively charged linear $\{\cdots N{\equiv}C{-}[Re_6Q_8(CN)_4]{-}C{\equiv}N{-}Ni2{-}N{\equiv}C{-}[Re_6Q_8(CN)_4]{-}C{\equiv}N\cdots\}_\infty$ chain (a) and a view along [001] of the crystal packing in $[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Q_8(CN)_6]Cl_2{\cdot}nH_2O$ (Q = Se and $n = 2$ for **2;** Q = Te and $n = 1$ for **3**) (b); all hydrogen and chalcogen atoms, water molecules and Cl^- anions have been omitted for clarity

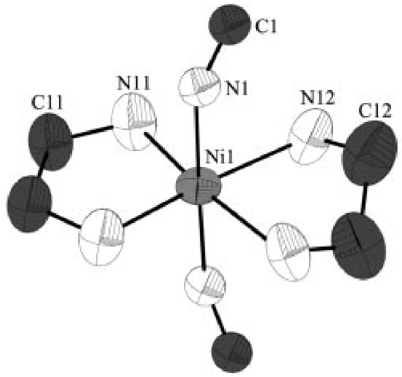

Figure 5. Ligand environment of Ni1 in **4**; displacement ellipsoids are drawn at the 50% probability level; all hydrogen atoms have been omitted for clarity

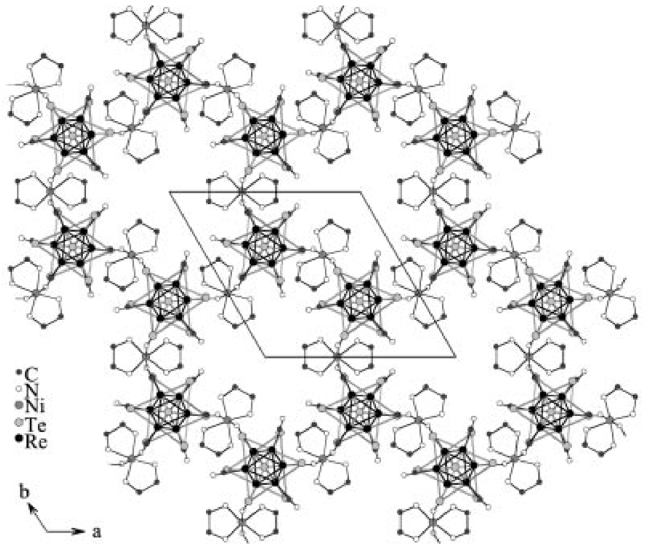

Figure 6. View along [001] of the crystal packing in $(NH_4)_2[\{Ni(en)_2\}_3\{Re_6Te_8(CN)_6\}_2]{\cdot}6H_2O$ (**4**); all hydrogen and tellurium atoms, ammonium cations and water molecules have been omitted for clarity

these values correspond to the c and $b/2$ cell parameters, respectively.

In the structure of compound **4** there is one crystallographically independent nickel cation that is located in a special position $3f$ (x, 0, 1/2; 0, x, 1/2; $-x$, $-x$, 1/2) and has crystallographically imposed C_2 symmetry. It is coordinated by two ethylenediamine molecules lying in the equatorial plane, with Ni−N(en) distances ranging from 2.09(3) to 2.16(3) Å. There are two independent rhenium atoms that belong to the same cluster core. The centre of the cluster anion coincides with the special crystallographic position $2d$ (1/3, 2/3, z; 2/3, 1/3, $-z$). Three CN groups from the same face of the Re_6 octahedron take part in the formation of negatively charged infinite wavy $[\{Ni(en)_2\}_3\{Re_6Te_8(CN)_6\}_2]^{2-}_{\infty\infty}$ layers by coordination to cationic $[Ni(en)_2]^{2+}$ units, which are coordinated by one more CN group from neighbouring clusters. The Ni−N(CN) distances are equal to 2.11(3) Å. Finally, the Ni atoms have an octahedral arrangement (Figure 5). In the structure the wavy layers lying in the ab plane are packed exactly above each other to form channels with approximate dimensions ranging from 4 Å to 7.2 Å (Figure 6).

Compound **5** contains one cluster anion built from six crystallographically independent rhenium atoms located in general positions and two crystallographically independent copper cations. Cu1 is located in a general position. Its coordination number is equal to five (4 + 1) resulting in the cationic complex $[Cu(NH_3)(en)_2]^{2+}$ (Figure 7a). Four coordination sites of Cu1 are occupied by two ethylenediamine molecules lying in the equatorial plane, with Cu1−N(en) distances in the range from 1.96(2) to 2.02(2) Å, and the fifth coordination site is occupied by ammonia, with a Cu1−$N(NH_3)$ distance equal to 2.32(2) Å. Cu2 is located in the special position $2c$ (0, 1/2, 0; 1/2, 1/2, 1/2) and has imposed $\bar{1}$ symmetry. The coordination number of Cu2 is six (or 4 + 2). Four coordination sites of Cu2 are occupied by two ethylenediamine molecules lying in the equatorial plane, with Cu2−N(en) distances ranging from 2.00(2) to 2.05(2) Å, and the two axial coordination sites are occupied by nitrogen atoms of CN groups of neighbouring clusters, with Cu2−N(CN) distances equal to 2.59(2) Å (Figure 7b). Such a ligand environment of Cu2 results in anionic $[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]^{6-}$ dimers (Figure 8a). The cationic complexes $[Cu(NH_3)(en)_2]^{2+}$ and cations Et_4N^+ compensate the negative charge of the $[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]^{6-}$ anions. Inside the structure of $(Et_4N)_2[Cu(NH_3)(en)_2]_2[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]{\cdot}2H_2O$ (Figure 8b) the anionic $[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]^{6-}$ dimers adopt two orientations. One of these orientations lies nearly along the (b + c) direction, whereas the second orientation is symmetry related and is situated nearly along the (b − c) direction.

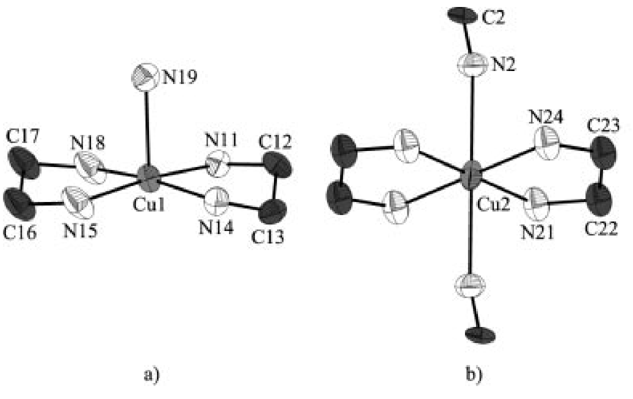

Figure 7. Ligand environment of Cu1 (a) and Cu2 (b) in **5**; displacement ellipsoids are drawn at the 30% probability level; all hydrogen atoms have been omitted for clarity

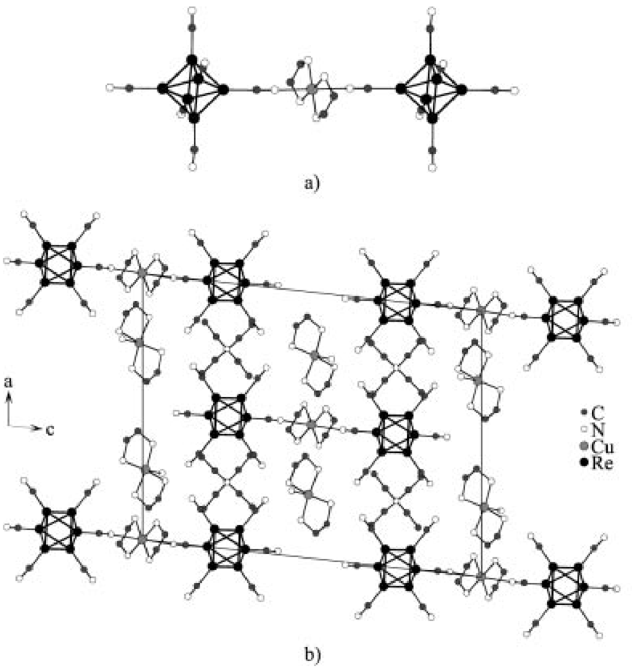

Figure 8. Structure of anionic dimer $[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]^{6-}$ (a) and view along [010] of the crystal packing in $(Et_4N)_2[Cu(NH_3)(en)_2]_2[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]\cdot 2H_2O$ (**5**) (b); all hydrogen and tellurium atoms and water molecules have been omitted for clarity

As was expected the use of ethylenediamine leads to a decrease in the overall number of M−NC−Re interactions and, hence, to a decrease in the dimensionality of the formed compounds compared to compounds reported earlier for $M^{2+}/[Re_6Q_8(CN)_6]^{4-}$ systems.[6−12] In general, the simultaneous presence of 3d transition metal cations and the chelating ligand ethylenediamine in solution generates different $[ML_{6-2x}(en)_x]^{2+}$ moieties, all of which can serve as building blocks.[27,28,33]

All the structures described here are based on the interaction of cationic $[M(en)_2]^{2+}$ moieties and $[Re_6Q_8(CN)_6]^{4-}$ (Q = Se, Te) anions. The different coordination of $[M(en)_2]^{2+}$ fragments by additional ligands, namely water, ammonia or nitrogen atoms from the cyano groups of the $[Re_6Q_8(CN)_6]^{4-}$ anion, leads to the structural diversity of the compounds. Compounds **1**−**3** have chain-like structures that differ in the binding modes between the cluster anions and metal centres. In **1** the cluster anion $[Re_6Te_8(CN)_6]^{4-}$ is coordinated by three $Mn(en)_2$ fragments (Figure 2), two of which in a *cis*-orientation relative to the Re_6 cluster core, form additional bonds with neighbouring cluster anions. Such binding leads to a zig-zag chain. The third coordinated $Mn(en)_2$ fragment is terminated by a water molecule.

In contrast to **1**, in isostructural **2** and **3** the nickel atoms are bound to *trans*-cyano groups of the anion, which leads to linear chains. Additionally, the nickel atoms are coordinated by four ammonia molecules. The $[Ni(NH_3)_2(en)_2]^{2+}$ cations serve as spacers and are located between the chains along with Cl^- anions, which adjust the charge balance in the structure. It is interesting that in the isomorphous compound $[Co(NH_3)_2(en)_2]_2[\{Co(en)_2\}Re_6Te_8(CN)_6]Cl_2\cdot H_2O$ the transition metal atoms in the polymeric chains are coordinated by ethylenediamine, not by ammonia.[28]

The inclusion of tetraethylammonium cations in **5** results in a change of connectivity in the structure. The structure does not contain infinite chains but only isolated anionic $[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]^{6-}$ dimer complexes. The formation of such fragments can be described formally as cleavage of $\{\cdots N{\equiv}C{-}[Re_6Q_8(CN)_4]{-}C{\equiv}N{-}M{-}N{\equiv}C{-}[Re_6Q_8(CN)_4]{-}C{\equiv}N\cdots\}_\infty$ chains similar to those found in **2** and **3** due to insertion of the more voluminous Et_4N^+ cations (Figure 9). The influence of cation size on the dimensionality of cyano-bridged clusters has been reported previously.[15,34]

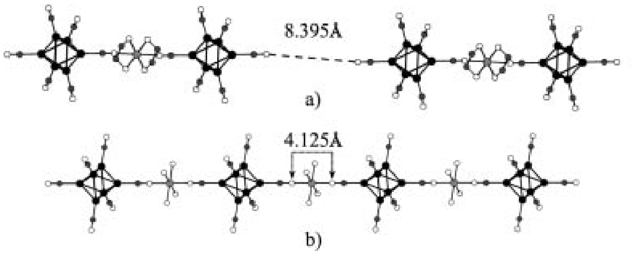

Figure 9. Arrangement of two anionic $[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]^{6-}$ dimers in **5** (a) in comparison with the chain fragment $\{\cdots N{\equiv}C{-}[Re_6Te_8(CN)_4]{-}C{\equiv}N{-}Ni2{-}N{\equiv}C{-}[Re_6Te_8(CN)_4]{-}C{\equiv}N\cdots\}_\infty$ of compound **3** (b)

On the other hand, the use of Bu_4NBr during crystallisation in the Ni/en/$[Re_6Te_8(CN)_6]^{4-}$ system led to intriguing results: the formation of **4** with a two-dimensional framework. Although Bu_4N^+ was not found in the structure of **4**, the presence of Bu_4N^+ in solution is crucial for the formation of this compound, otherwise chain-like compound **3** is formed. In the structure **4** the corrugated $[\{Ni(en)_2\}_3\{Re_6Te_8(CN)_6\}_2]^{2-}_{\infty\infty}$ sheets are stacked exactly above each other. This stacking gives large accessible channels directed along the *c* axis. These channels have a variable profile with dimensions vary from about 4 Å to 7.2 Å based on the estimated van der Waals radii. The CH_2 groups of the ethylenediamine molecules coordinated to the nickel atoms form the narrow section of channels that separate large spherical cavities with a volume of 631 Å^3 (based on calculations performed with PLATON[35]). The cavities centered near the origin (0,0,0) are decorated by six nitrogen atoms from cyano groups of cluster anions. They are filled by solvate water molecules and ammonium cations for charge balance of the framework.

Conclusion

The use of the simplest chelating ligand — ethylenediamine — during co-crystallisation of $[Re_6Q_8(CN)_6]^{4-}$ (Q = Se, Te) with 3d transition metals has resulted in the structural diversity of the formed compounds.

Experimental Section

General: Elemental analyses for C, H, N and S (Carlo Erba 1106) were performed in the Laboratory of Microanalysis of the Institute of Organic Chemistry, Novosibirsk. IR spectra were measured on KBr disks with a Bruker IFS-85 Fourier spectrometer. The starting cluster compounds were synthesised as described previously: $K_4[Re_6Se_8(CN)_6]\cdot3.5H_2O$ was prepared from polymeric $Re_6Se_8Br_2$;[3] $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$ was prepared by adding CsCl to an aqueous solution of the reaction product of polymeric Re_6Te_{15} with molten KCN.[5]

$[\{Mn(H_2O)(en)_2\}\{Mn(en)_2\}Re_6Te_8(CN)_6]\cdot3H_2O$ (1): The reaction was carried out by layering a solution of $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$ (2.0 mg, 0.7 μmol) in water (1 mL) on top of a solution of $Mn(OAc)_2\cdot4H_2O$ (7 mg, 0.03 mmol) and ethylenediamine (0.01 mL, 0.15 mmol) in glycerol (1 mL). After two weeks, dark red-brown crystals were obtained. These crystals were filtered off and dried on filter paper. The yield was quantitative based on Re. IR: ν_{CN} = 2052s, 2098s and 2112m cm^{-1}. $C_{14}H_{40}Mn_2N_{14}O_4Re_6Te_8$ (2716.5): calcd. C 6.19, H 1.48, N 7.22; found C 6.04, H 1.52, N 7.13.

$[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Se_8(CN)_6]Cl_2\cdot2H_2O$ (2): In a similar manner, layering a solution of $K_4[Re_6Se_8(CN)_6]\cdot3.5H_2O$ (2.0 mg, 0.94 μmol) in aqueous ammonia (1 mL) on top of a solution of $NiCl_2\cdot6H_2O$ (7 mg, 0.03 mmol) and ethylenediamine (0.002 mL, 0.03 mmol) in glycerol (1 mL) afforded dark red-brown crystals. The yield was quantitative based on Re. $C_{14}H_{60}Cl_2N_{22}Ni_3O_2Re_6Se_8$ (2564.7): calcd. C 6.56, H 2.36, N 12.02; found C 6.61, H 2.24, N 11.97.

$[Ni(NH_3)_2(en)_2]_2[\{Ni(NH_3)_4\}Re_6Te_8(CN)_6]Cl_2\cdot H_2O$ (3): This compound was synthesised as for **2** by substituting $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$ (2.0 mg, 0.7 μmol) for $K_4[Re_6Se_8(CN)_6]\cdot3.5H_2O$. The resultant dark red-brown crystals were filtered off and dried on filter paper. The yield was quantitative based on Re. $C_{14}H_{58}Cl_2N_{22}Ni_3ORe_6Te_8$ (2935.8): calcd. C 5.73, H 1.99, N 10.50; found C 5.73, H 1.87, N 10.44.

$(NH_4)_2[\{Ni(en)_2\}_3\{Re_6Te_8(CN)_6\}_2]\cdot6H_2O$ (4): A solution of $NiCl_2\cdot6H_2O$ (3.33 mg, 0.014 mmol) and ethylenediamine (1.9 μL, 0.028 mmol) in aqueous ammonia (0.5 mL) was added to a solution of $Cs_4[Re_6Te_8(CN)_6]\cdot2H_2O$ (20 mg, 7.0 μmol) and Bu_4NBr (11.28 mg, 0.035 mmol) in aqueous ammonia (10 mL). The resultant solution was kept in a tightly closed vessel at room temperature for two weeks, during which time dark red-brown crystals formed. These crystals were filtered off and dried on filter paper. The yield was quantitative based on Re. IR: ν_{CN} = 2051s, 2091w, 2119m and 2133w cm^{-1}. $C_{12}H_{34}N_{13}Ni_{1.5}O_3Re_6Te_8$ (2634.57): calcd. C 5.47, H 1.30, N 6.91; found C 5.60, H 1.21, N 6.84.

$(Et_4N)_2[Cu(NH_3)(en)_2]_2[\{Cu(en)_2\}\{Re_6Te_8(CN)_6\}_2]\cdot2H_2O$ (5): A solution of $CuCl_2\cdot2H_2O$ (12 mg, 0.07 mmol) and ethylenediamine (0.047 mL, 0.7 mmol) in aqueous ammonia (1.5 mL) was added to

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

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{14}H_{40}Mn_2$-$N_{14}O_4Re_6Te_8$	$C_{14}H_{60}Cl_2$-$N_{22}Ni_3O_2Re_6Se_8$	$C_{14}H_{58}Cl_2N_{22}$-$Ni_3ORe_6Te_8$	$C_{12}H_{34}N_{13}$-$Ni_{1.5}O_3Re_6Te_8$	$C_{20}H_{49}Cu_{1.5}N_{14}$-$ORe_6Te_8$
Formula mass	2716.48	2564.68	2935.79	2634.57	2735.06
Crystal system	monoclinic	monoclinic	monoclinic	trigonal	monoclinic
Space group	$P2_1/n$	$Cmmm$	$Cmmm$	$P321$	$P2/n$
a [Å]	10.7940(1)	14.408(5)	14.3725(3)	15.794(5)	19.445(5)
b [Å]	16.8011(3)	16.155(5)	16.4050(3)		11.534(5)
c [Å]	24.6467(5)	11.822(5)	12.1078(3)	10.646(5)	24.870(5)
β [°]	92.055(1)				96.328(5)
V [Å^3]	4466.8(1)	2752(2)	2854.8(1)	2300(2)	5544(3)
Z	4	2	2	2	4
$\rho_{calcd.}$ [g·cm^{-3}]	3.957	3.095	3.347	3.755	3.298
Crystal size [mm]	0.02×0.03×0.06	0.20 × 0.28 × 0.35	0.12 × 0.13 × 0.16	0.03 × 0.04 × 0.07	0.05 × 0.05 × 0.15
θ_{max} [°]	27.495	35.005	34.945	27.079	30.040
Exp. hkl limits	$-14 \le h \le 13$	$-23 \le h \le 23$	$0 \le h \le 23$	$-20 \le h \le 20$	$-27 \le h \le 27$
	$-19 \le k \le 21$	$-26 \le k \le 20$	$-26 \le k \le 26$	$-20 \le k \le 20$	$-16 \le k \le 15$
	$-31 \le l \le 30$	$-19 \le l \le 18$	$-15 \le l \le 19$	$-12 \le l \le 13$	$-27 \le l \le 35$
Refl. collected/unique	49870/10235	25142/3338	26490/3451	27676/3402	67318/16189
$R_{(int)}$	0.06	0.13	0.06	0.10	0.07
μ [cm^{-1}]	218.91	195.66	177.65	213.25	177.62
Max./min. transm.	0.51/0.27	0.11/0.01	0.25/0.14	0.53/0.45	0.51/0.21
Refined parameters/ refl. with $F_o \ge 4\sigma(F)$	351/4350	88/1776	89/1723	83/1207	411/6985
$R(F)$[a]/$R_w(F^2)$[b]	0.0295/0.0624	0.0336/0.0556	0.0310/0.0481	0.0364/0.0485	0.0441/0.0718
$\Delta\rho_{max.}/\Delta\rho_{min.}$ [e·Å^{-3}]	1.50/−1.71	2.22/−2.83	3.09/−2.34	2.97/−2.83	4.72/−3.13

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$.

a solution of $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ (20 mg, 7.0 µmol) and Et_4NBr (7.35 mg, 0.035 mmol) in aqueous ammonia (10 mL). The resultant solution was kept in a tightly closed vessel at room temperature for two weeks, during which time dark red-brown crystals formed. These crystals were filtered off and dried on filter paper. The yield was quantitative based on Re. IR: ν_{CN} = 2074s, 2103m and 2141m cm^{-1}. $C_{20}H_{49}Cu_{1.5}N_{14}ORe_6Te_8$ (2735.1): calcd. C 8.78, H 1.81, N 7.17; found C 8.83, H 1.62, N 7.15.

X-ray Crystallographic Study: Selected single crystals were mounted, as usual, on the top of a glass fibre. Diffraction data were collected at room temperature (293 K) with a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Experimental details for complexes **1–5** are given in Table 1. The data processing was performed by the Kappa CCD analysis software;[36] the lattice constants were refined by least-square refinement. Absorption corrections based on the crystal shapes were applied to the data sets with the ANALYTICAL program[37,38] for all structures. Structure solution and refinement: Complexes **1** and **5** crystallised in the monoclinic system. The systematic absences led to the *P*2$_1$/*n and P*2/*n* space groups, respectively. For **2** and **3**, the observed systematic absences suggested an orthorhombic crystal system with a *C* lattice. Among the possible space groups, the refinement procedure allowed us to determine unambiguously the *Cmmm* space group. Complex **4** crystallised in the trigonal system with a *P* lattice. The systematic absences led to the *P*321 group. The structures were solved by direct methods (SIR97 program[39]) combined with Fourier-difference syntheses and refined against *F* using reflections with $I > 3\sigma(I)$ (CRYSTALS program[40]). All atoms were refined anisotropically. CCDC-234060 to -234064 (**1–5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: + 44-1223-336-033; or deposit@ccdc.cam.ac.uk).

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