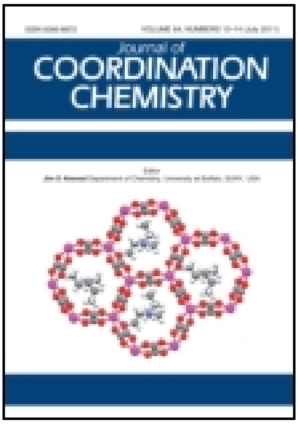
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:28
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

# A 1-D cyano-bridged coordination polymer, $[Ni(NH_3)_6]_2[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]\cdot 8H_2O$: reactivity studies of dodecanuclear rhenium cluster anion $[Re_{12}CS_{17}(CN)_6]^{6-}$ in Ni(II)-ammonia system

Yakov M. Gayfulin [a] , Anton I. Smolentsev [a] & Yuri V. Mironov [a]
[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences , Akad. Lavrentiev prosp., 3, Novosibirsk 630090, Russian Federation
Published online: 04 Nov 2011.

To cite this article: Yakov M. Gayfulin , Anton I. Smolentsev & Yuri V. Mironov (2011) A 1-D cyano-bridged coordination polymer, $[Ni(NH_3)_6]_2[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]\cdot 8H_2O$: reactivity studies of dodecanuclear rhenium cluster anion $[Re_{12}CS_{17}(CN)_6]^{6-}$ in Ni(II)-ammonia system, Journal of Coordination Chemistry, 64:21, 3832-3840, DOI: 10.1080/00958972.2011.632005

To link to this article: http://dx.doi.org/10.1080/00958972.2011.632005

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

*Journal of Coordination Chemistry*
Vol. 64, No. 21, 10 November 2011, 3832–3840

Taylor & Francis
Taylor & Francis Group

# A 1-D cyano-bridged coordination polymer, $[Ni(NH_3)_6]_2[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]\cdot 8H_2O$: reactivity studies of dodecanuclear rhenium cluster anion $[Re_{12}CS_{17}(CN)_6]^{6-}$ in Ni(II)-ammonia system

YAKOV M. GAYFULIN, ANTON I. SMOLENTSEV* and YURI V. MIRONOV

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Akad. Lavrentiev prosp., 3, Novosibirsk 630090, Russian Federation

(*Received 11 August 2011; in final form 29 September 2011*)

A cyano-bridged coordination polymer, $[Ni(NH_3)_6]_2[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]\cdot 8H_2O$, has been synthesized by reaction between concentrated aqueous ammonia solution of $NiCl_2$ and aqueous solution of $K_6[Re_{12}CS_{17}(CN)_6]$. The compound has been characterized by single crystal X-ray diffraction, IR-spectroscopy and EDS analysis. The compound adopts 1-D structure, which consists of anionic chains $[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]_n^{4n-}$, discrete cations $[Ni(NH_3)_6]^{2+}$ and crystal waters bonded together by hydrogen bonds. The influence of reagent concentrations on composition and structure of the resultant product has also been studied and discussed.

*Keywords*: Rhenium; Dodecanuclear cluster complex; Coordination polymer; Crystal structure

## 1. Introduction

The chemistry of rhenium chalcocyanide cluster complexes with transition or post-transition metals has attracted attention. The most important feature of these complexes is a well-known capability of terminal $CN^-$ to serve as ambidentate ligands with potential to form a variety of cyano-bridged structures with different dimensionalities and architectures – from discrete molecular to 1-D, 2-D, and 3-D polymers. Particularly, for tetranuclear and hexanuclear chalcocyanide clusters, $[Re_4Q_4(CN)_{12}]^{4-}$ and $[Re_6Q_8(CN)_6]^{n-}$ ($Q = S$, Se, Te, $n = 3$, 4), a number of complexes has been synthesized to date and their crystal structures and properties studied in detail [1–14].

Several years ago, rhenium sulfido-cyanide clusters $[Re_{12}CS_{17}(CN)_6]^{n-}$ ($n = 6$, 8) featuring unique crystal structures and a reversible redox two-electron transformation $\{[Re_{12}CS_{17}(CN)_6]^{6-} \leftrightarrow [Re_{12}CS_{17}(CN)_6]^{8-}\}$, containing a carbon-centered dodecanuclear (bioctahedral) cluster, were synthesized [15]. Changes in the carbon-centered fragment $\{Re_6C\}$, taking place during this transformation, gave the possibility of these

---

*Corresponding author. Email: smolentsev@ngs.ru

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.632005

complexes as a perspective molecular switch [16]. From another point of view, an air stable highly negative (6−) anion may be used as a block for the preparation of cyano-bridged coordination polymers. The first studies of $[Re_{12}CS_{17}(CN)_6]^{6-}$ coordinating transition metal ions (using ammonia solutions of $NiCl_2$ as an example system) resulted in isolation and characterization of two cyano-bridged compounds, $[\{Ni(NH_3)_4\}\{Ni(NH_3)_5\}_2\{Re_{12}CS_{17}(CN)_6\}] \cdot 7H_2O$ adopting a chain structure and $[Ni(NH_3)_6]_3[\{Ni(NH_3)_4\}_3\{Re_{12}CS_{17}(CN)_6\}_2] \cdot 21H_2O$ with a structure containing dimeric fragments $[\{Ni(NH_3)_4\}_3\{Re_{12}CS_{17}(CN)_6\}_2]^{6-}$ [17]. These new compounds demonstrated the CN–Ni–NC intercluster bridge bonding similar to that found in cyano-complexes based on $\{Re_6Q_8\}$ and $\{Re_4Q_4\}$ cluster cores [5–8]. For similar copper-containing systems the anion, $[Re_{12}CS_{17}(CN)_6]^{6-}$, gave two compounds with an ionic structure, $[Cu(NH_3)_5]_3[Re_{12}CS_{17}(CN)_6] \cdot 8H_2O$ and $[Cu(NH_3)(en)_2][Cu(NH_3)_3(en)]_2[Re_{12}CS_{17}(CN)_6] \cdot 5H_2O$ (en = ethylenediamine) [18].

In continuation of our studies of the $Ni^{2+}$–ammonia–dodecanuclear rhenium cluster anion, we herein report the synthesis and structural characterization of a new cluster complex with a polymer chain structure, $[Ni(NH_3)_6]_2[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}] \cdot 8H_2O$ (**1**).

## 2. Experimental

### 2.1. *Materials and instruments*

All reagents were used as purchased without purification. $ReS_2$ was synthesized from elements in a sealed quartz tube at 650°C. The starting compound $K_6[Re_{12}CS_{17}(CN)_6] \cdot 20H_2O$ was prepared from $ReS_2$ and KCN as described [15]. Energy Dispersive Spectroscopy (EDS) of the title compound was performed on a Scanning Electron Microscope (SEM) JEOL 6400. Infrared spectrum in KBr pellet was recorded using a Bruker Scimitar FTS 2000 spectrometer from 4000–375 $cm^{-1}$.

### 2.2. *Synthesis and characterization*

Synthesis of **1** was carried out in a thin glass tube constricted in the middle. Nickel(II) chloride hexahydrate (4 mg, 0.0168 mmol) was dissolved in 4 mL of concentrated aqueous ammonia. This solution was then layered over 4 mL of an aqueous solution containing 4 mg (0.0012 mmol) of $K_6[Re_{12}CS_{17}(CN)_6] \cdot 20H_2O$. Five days later, black needle-shaped crystals suitable for X-ray investigation formed on the walls of the tube at its upper part. The crystals undergo slow decomposition in air. Yield: 4 mg (93%). EDS showed the following Ni : Re : S ratios: 3.0 : 12.0 : 16.5. FT-IR (KBr pellet, $cm^{-1}$): 414.7(w), 462.6(w), 717.2(w), 1206.7(s), 1592.1(s), 2130.3(s), 2157.9(m), 3129.7(w), 3263.5(w), 3352.5(w).

### 2.3. *Crystal structure determination*

A crystal of **1** was selected under a microscope and then mounted to the tip of a thin glass fiber with epoxy resin. X-ray intensity data were collected on a Bruker X8 Apex

Table 1. Crystal data, data collection and refinement parameters for **1**.

| | |
|---|---|
| Chemical formula | $[Ni(NH_3)_6]_2[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}] \cdot 8H_2O$ |
| Brutto formula | $C_7H_{64}N_{22}Ni_3O_8Re_{12}S_{17}$ |
| Formula weight | 3540.35 |
| Temperature (K) | 150(2) |
| Crystal size ($mm^3$) | $0.12 \times 0.06 \times 0.02$ |
| Crystal system | Orthorhombic |
| Space group | *Pmma* |
| Unit cell dimensions (Å) | |
| $a$ | 30.8904(8) |
| $b$ | 10.8804(3) |
| $c$ | 9.5420(3) |
| Volume ($Å^3$), $Z$ | 3207.07(16), 2 |
| $D_{\mathrm{Calcd}}$ ($g\ cm^{-3}$) | 3.605 |
| Absorption coefficient ($mm^{-1}$) | 23.995 |
| $\theta$ range (°) | 1.87–30.04 |
| Reflections collected | 28,169 |
| Unique reflections | 5018 ($R_{\mathrm{int}} = 0.063$) |
| Observed reflections | 3834 ($I > 2\sigma(I)$) |
| Parameters refined | 259 |
| $R[F^2 > 2\sigma(F^2)]$ | $R_1 = 0.034$<br>$wR_2 = 0.073$ |
| $R(F^2)$ (all data) | $R_1 = 0.054$<br>$wR_2 = 0.078$ |
| Goodness-of-fit on $F^2$ | 1.048 |
| $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ ($e\ Å^{-3}$) | 2.10 and −3.35 |

CCD diffractometer at 150(2) K using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). The standard technique was used ($\omega$- and $\phi$-scans of narrow frames). Data reduction and multi-scan absorption were carried out using SADABS [19]. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELX-97 software package [20]. All non-hydrogen atoms were refined anisotropically. Hydrogens of $NH_3$ were calculated by geometrical methods and refined as riding; hydrogens of water were not located. Residual electron density was found between −3.35 and 2.10 e Å$^{-3}$. Crystallographic data together with selected refinement details are given in table 1. Selected bond lengths are listed in table 2.

## 3. Results and discussion

### 3.1. *Synthesis*

Previous studies on the chemical behavior of tetra- and hexanuclear rhenium chalcocyanide cluster anions in aqueous and ammonia solutions containing transition metal ions allowed us to expect similar behavior for a newly synthesized dodecanuclear anion. Concentrated ammonia solutions are in certain cases more suitable for preparation of cyano-bridged coordination polymers [21–26]. In this case the polymerization is slowed by formation of $[M(NH_3)_n]^{2+}$, in which all coordination sites of the metal are occupied by $NH_3$, thereby making difficult coordination of ambidentate $CN^-$. For dodecanuclear cluster complexes, mixing aqueous solutions of $K_6[Re_{12}CS_{17}(CN)_6]$ and $MCl_2$ (M = Ni, Cu) led to quick precipitation of insoluble amorphous products,

Table 2. Selected interatomic distances (Å) for **1**.

| | | | |
|---|---|---|---|
| Re(1)–Re(2) | 2.6012(5) | Re(4)–S(4) | 2.398(3) |
| Re(1)–Re(3) | 2.6229(5) | Re(4)–S(7) | 2.369(3) |
| Re(2)–Re(2)$^{i}$ | 2.5907(6) | Re(1)–C(1) | 2.093(11) |
| Re(2)–Re(3) | 2.6297(4) | Re(2)–C(2) | 2.112(9) |
| Re(2)–Re(4) | 2.6272(5) | Re(3)–C(3) | 2.134(5) |
| Re(3)–Re(3)$^{i}$ | 2.6929(6) | Re(4)–C(3) | 2.117(10) |
| Re(3)–Re(3)$^{ii}$ | 2.9054(6) | C(1)–N(1) | 1.163(15) |
| Re(3)–Re(4) | 2.6933(4) | C(2)–N(2) | 1.142(12) |
| Re(4)–Re(4)$^{iii}$ | 2.9058(8) | Ni(1)–N(1) | 2.089(10) |
| Re(1)–S(1) | 2.407(2) | Ni(1)–N(11) | 2.080(11) |
| Re(1)–S(3) | 2.411(3) | Ni(1)–N(12) | 2.122(14) |
| Re(1)–S(5) | 2.392(3) | Ni(2)–N(21) | 2.12(3) |
| Re(2)–S(1) | 2.404(2) | Ni(2)–N(22) | 2.11(4) |
| Re(2)–S(2) | 2.397(2) | Ni(2)–N(23) | 2.19(3) |
| Re(2)–S(3) | 2.413(2) | Ni(2)–N(24) | 2.18(2) |
| Re(2)–S(4) | 2.408(2) | Ni(2)–N(25) | 2.15(2) |
| Re(3)–S(1) | 2.402(2) | Ni(3)–N(31) | 2.12(2) |
| Re(3)–S(2) | 2.428(2) | Ni(3)–N(32) | 2.21(4) |
| Re(3)–S(5) | 2.430(2) | Ni(3)–N(32) | 2.21(3) |
| Re(3)–S(6) | 2.380(2) | Ni(3)–N(34) | 2.15(2) |
| Re(4)–S(2) | 2.424(2) | Ni(3)–N(35) | 2.179(15) |

Equivalent positions: $^{(i)}x, 1-y, z$; $^{(ii)}1/2-x, y, z$; $^{(iii)}1/2-x, 1-y, z$.

unsuitable for X-ray diffraction analysis, whereas in ammonia, the 1-D coordination polymer $[\{Ni(NH_3)_4\}\{Ni(NH_3)_5\}_2\{Re_{12}CS_{17}(CN)_6\}]\cdot 7H_2O$, as well as the dimeric compound, $[Ni(NH_3)_6]_3[\{Ni(NH_3)_4\}_3\{Re_{12}CS_{17}(CN)_6\}_2]\cdot 21H_2O$, and the ionic compound, $[\{Ni(NH_3)_6\}_3\{Re_{12}CS_{17}(CN)_6\}]$, were synthesized [17] (figure 1). In the present article, we describe a new 1-D polymer, **1**, obtained in this system by varying the initial concentrations of reagents. The controlling parameters here are: first, the overall concentrations of the polymer-forming counterions in solution that influences the speed of the reaction; and second, the ratio of these counterions.

It is interesting to compare the synthetic conditions corresponding to **1** with those known from our previous studies (ammonia concentrations are assumed to be constant in all experiments). **1** was formed at the lowest initial concentrations of reagents, $1\,\mathrm{mgmL^{-1}}$ ($4.2\cdot 10^{-3}$ M) of $NiCl_2\cdot 6H_2O$ and $1\,\mathrm{mgmL^{-1}}$ ($2.8\cdot 10^{-4}$ M) of $K_6[Re_{12}CS_{17}(CN)_6]\cdot 20H_2O$. $[\{Ni(NH_3)_4\}\{Ni(NH_3)_5\}_2\{Re_{12}CS_{17}(CN)_6\}]\cdot 7H_2O$ was obtained at concentrations of $10\,\mathrm{mgmL^{-1}}$ ($4.2\cdot 10^{-2}$ M) and $4\,\mathrm{mgmL^{-1}}$ ($1.1\cdot 10^{-3}$ M). $[Ni(NH_3)_6]_3[\{Ni(NH_3)_4\}_3\{Re_{12}CS_{17}(CN)_6\}_2]\cdot 21H_2O$ was formed under the same conditions except much longer time was needed for crystal growth (about a month *versus* several days). Further increasing of cluster salt concentration to $10\,\mathrm{mgmL^{-1}}$ ($2.8\cdot 10^{-3}$ M) led not to the formation of cyano-bridged polymers, but instead afforded the unstable compound with an ionic structure, $[\{Ni(NH_3)_6\}_3\{Re_{12}CS_{17}(CN)_6\}]$.

These fragmentary data cannot provide full understanding of how the initial concentrations of reagents influence the composition and structure of the described products. One can only see that assembly of a polymeric species is observed at relatively low concentrations. A high concentration of cluster anions causes quick precipitation of insoluble crystalline product (discrete ionic structure), whereas relatively slow cyanide bridging does not occur. The excess of $Ni^{2+}$ (3–8 times for the described experiments) may be another factor assisting polymer formation.

In order to clarify this situation, a wide range of reagent concentrations has been investigated in the present work. The concentrations of the $Ni^{2+}$ cations were varied

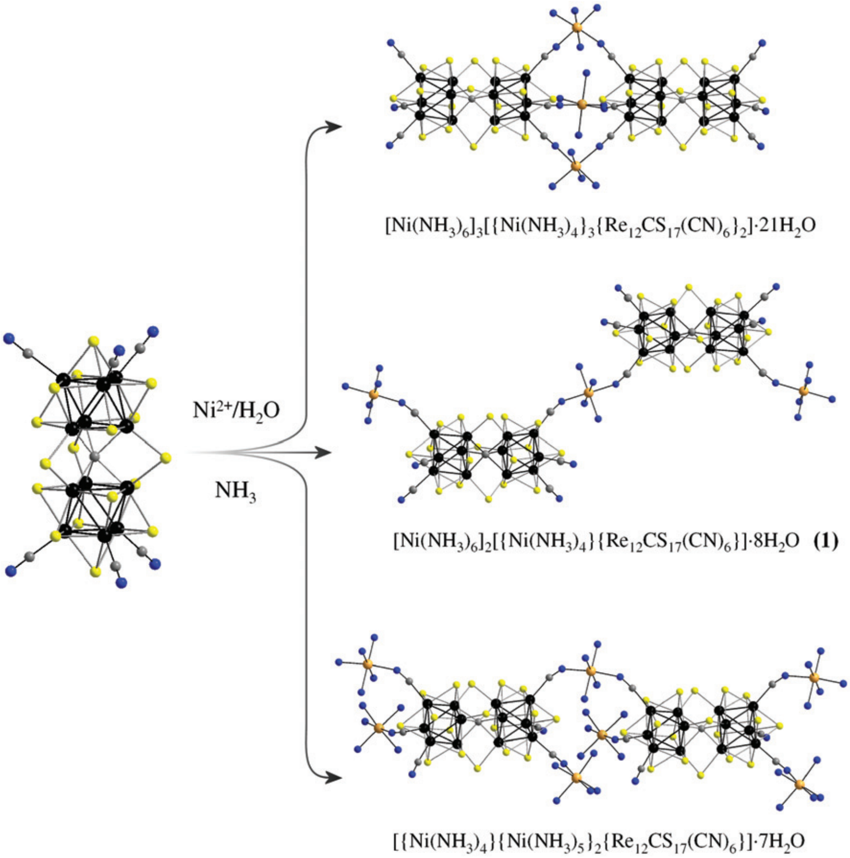


Figure 1. Reaction between aqueous ammonia solution of $NiCl_2$ and aqueous solution of $K_6[Re_{12}CS_{17}(CN)_6]$ showing the products obtained to date. The ionic compound $[\{Ni(NH_3)_6\}_3\{Re_{12}CS_{17}(CN)_6\}]$ is omitted due to the poor quality of the structural data.

from 0.5 mgmL$^{-1}$ ($2.1\cdot10^{-3}$ M) to 30 mgmL$^{-1}$ ($1.3\cdot10^{-1}$ M). The concentrations of the $[Re_{12}CS_{17}(CN)_6]^{6-}$ anion were varied from 0.5 mgmL$^{-1}$ ($1.4\cdot10^{-4}$ M) to 20 mgmL$^{-1}$ ($5.6\cdot10^{-3}$ M). In each case, if formation of single crystals was observed, the unit cell measurements were performed to identify the product of the reaction. Finally, the following approximate ranges of concentrations have been determined: at 0.5–5 mgmL$^{-1}$ ($2.1\cdot10^{-3}$ – $2.1\cdot10^{-2}$ M) of $Ni^{2+}$ cations and 0.5–5 mgmL$^{-1}$ ($1.4\cdot10^{-4}$–$1.4\cdot10^{-3}$ M) of cluster anions, **1** is formed. At 5–20 mgmL$^{-1}$ ($2.1\cdot10^{-2}$ – $8.4\cdot10^{-2}$ M) of $Ni^{2+}$ cations and 1–5 mgmL$^{-1}$ ($2.8\cdot10^{-4}$ – $1.4\cdot10^{-3}$ M) of cluster anions, $[\{Ni(NH_3)_4\}\{Ni(NH_3)_5\}_2\{Re_{12}CS_{17}(CN)_6\}]\cdot7H_2O$ is formed (which on standing turns into $[Ni(NH_3)_6]_3[\{Ni(NH_3)_4\}_3\{Re_{12}CS_{17}(CN)_6\}_2]\cdot21H_2O$); at cation and anion concentrations higher than 20 mgmL$^{-1}$ ($8.4\cdot10^{-2}$ M) and 10 mgmL$^{-1}$ ($2.8\cdot10^{-3}$ M), respectively, $[\{Ni(NH_3)_6\}_3\{Re_{12}CS_{17}(CN)_6\}]$ is formed.

### 3.2. *IR-spectroscopy*

Peak assignments in the vibrational spectrum of **1** have been made according to literature values [27]. IR bands for antisymmetric and symmetric stretching vibrations

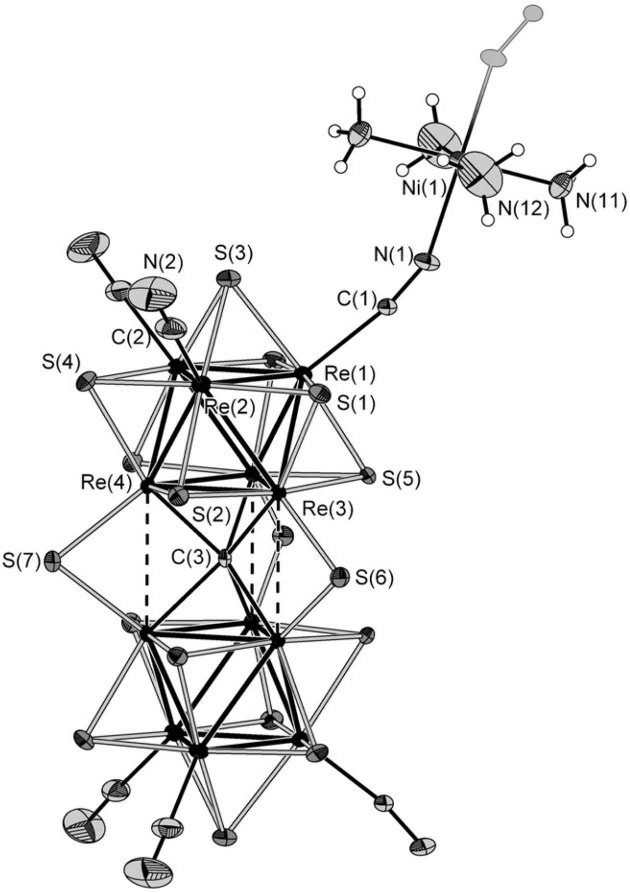


Figure 2. A fragment of **1** showing a basic building block of the polymeric chain $[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]_n^{4n-}$, with atom numbering scheme and thermal ellipsoids drawn at the 50% probability level.

of $NH_3$, $NH_3$ asymmetric deformation, $NH_3$ symmetric deformation, and $NH_3$ vibrations appeared at 3400–3100 and at 1592, 1206 and 717 $cm^{-1}$, respectively. Presence of a broad band at 3500–3600 $cm^{-1}$ corresponds to the presence of lattice waters. Strong band at 2130 $cm^{-1}$ was attributed to the vibrations of CN bonds.

### 3.3. *Crystal structure*

Single crystal X-ray structure determination revealed that the unit cell of **1** consists of four discrete $[Ni(NH_3)_6]^{2+}$ cations, two $[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]^{4-}$ anionic fragments and sixteen lattice waters. The $[Re_{12}CS_{17}(CN)_6]^{6-}$ bioctahedral cluster anion consists of four asymmetric Re's, seven sulfurs, one carbon and one $CN^-$ (figure 2). These atoms are located in the following special positions: $m$ point symmetry ($x$, 1/2, $z$) for C(1), N(1), Re(1), Re(4), S(3), S(4), S(5); $m$ symmetry (1/4, $y$, $z$) for S(6), and $mm2$ symmetry (1/4, 1/2, $z$) for C(3) and S(7). Remaining cluster anion atoms, Re(2), Re(3), S(1) and S(2), occupy a general position ($x$, $y$, $z$). The Re–Re interatomic

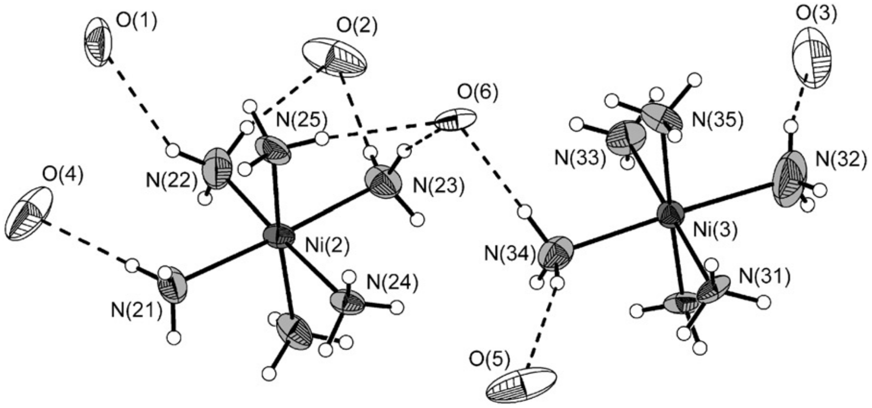


Figure 3. Discrete $[Ni(NH_3)_6]^{2+}$ cations surrounded by multiple waters of crystallization. The dashed lines represent hydrogen bonds; thermal ellipsoids are drawn at the 50% probability level.

distances have the following mean values (Å): 2.598(5) for $Re^{out}$–$Re^{out}$, 2.693(3) for $Re^{in}$–$Re^{in}$ and 2.627(3) for $Re^{out}$–$Re^{in}$ (where $Re^{out}$ and $Re^{in}$ belong to opposite "outward" and "inward" faces of the $\{Re_6\}$ octahedron with regard to $\mu_6$-C). The three longer distances Re…Re in a trigonal $\{Re_6C\}$ prism are all equal to 2.9058(8) Å. The mean values of Re–$\mu_6$-C, Re–$C_{CN}$, Re–$\mu_2$-S and Re–$\mu_3$-S distances are 2.128(9), 2.108(10), 2.376(6), and 2.41(1) Å, respectively, in agreement with analogous values found for previously studied compounds containing $[Re_{12}CS_{17}(CN)_6]^{6-}$ [15–18].

In the crystal structure of **1**, $[Re_{12}CS_{17}(CN)_6]^{6-}$ participates in formation of an anionic zigzag chain running along the *a* axis of the unit cell; the "monomer" unit can be described as $[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]^{4-}$. Each repeating fragment includes Ni bonded to two nitrogens of cyano *trans* to one another and four ammonias. Thus, the Ni which participates in CN–Ni–NC bridge formation is centrosymmetrically surrounded by six nitrogens in a slightly distorted octahedral coordination geometry.

The structure contains two types of crystallographically unique cations $[Ni(NH_3)_6]^{2+}$ having Ni (located at the ($x$, 0, $z$) special positions, *m* symmetry) in a slightly distorted octahedral coordination environment (figure 3). The cations are each disordered over two sites with equal (50%) occupancies. Second coordination sphere interactions include multiple weak N–H…$N_{CN}$, N–H…O, O–H…$N_{CN}$ and O–H…O hydrogen bonds between $NH_3$ and CN, and lattice water molecules, with mean distances N…$N_{CN}$, N…O, O…$N_{CN}$ and O…O of 3.2(2), 3.2(1), 2.9(1), and 3.1(2) Å, respectively. The spatial disposition of the waters is also interesting appearing mostly (12 of 16 unit cell molecules) between $[Ni(NH_3)_6]^{2+}$ cations, lying in planes parallel to the *ab* and *ac* crystallographic planes (figure 4). Such a complex system of non-covalent interactions, along with electrostatic interactions, plays a significant role in the crystal lattice stabilization.

## 4. Conclusions

In the present study, dodecanuclear rhenium cluster anion $[Re_{12}CS_{17}(CN)_6]^{6-}$ effectively serves as a building block for construction of cyano-bridged

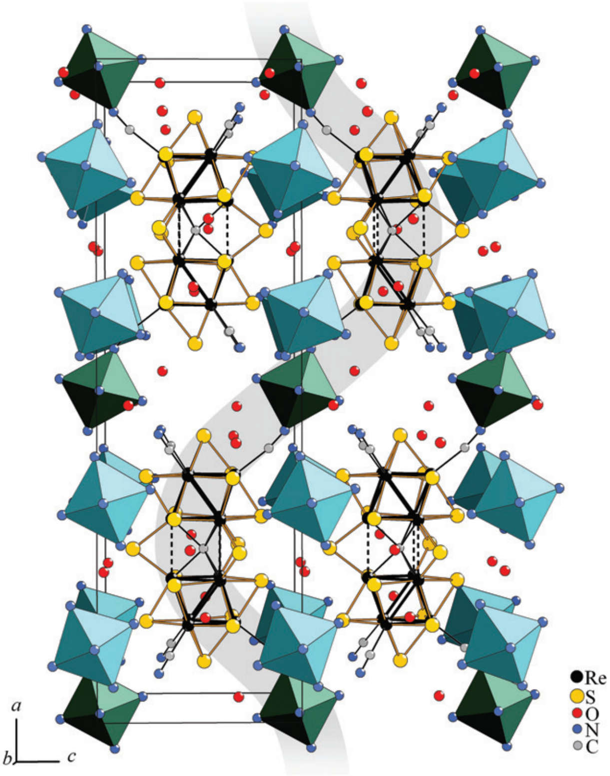


Figure 4. A perspective view of **1**. Light gray and dark gray octahedra represent, respectively, discrete $[Ni(NH_3)_6]^{2+}$ cations and a $\{Ni(NH_3)_4(CN)_2\}$ fragment of the polymeric chain (highlighted by a strip). Hydrogens are omitted for clarity.

coordination polymers. In addition to $[\{Ni(NH_3)_4\}\{Ni(NH_3)_5\}_2\{Re_{12}CS_{17}(CN)_6\}]\cdot 7H_2O$, $[Ni(NH_3)_6]_3[\{Ni(NH_3)_4\}_3\{Re_{12}CS_{17}(CN)_6\}_2]\cdot 21H_2O$ and $[\{Ni(NH_3)_6\}_3\{Re_{12}CS_{17}(CN)_6\}]$, a fourth new compound, **1**, has been isolated and structurally investigated. Single crystal X-ray structure determination reveals the presence of zigzag anionic chains $[\{Ni(NH_3)_4\}\{Re_{12}CS_{17}(CN)_6\}]_n^{4n-}$ electrostatically compensated by discrete $[Ni(NH_3)_6]^{2+}$, and lattice waters. In the studied system, at all reagent concentrations examined, no other compounds are formed. However, bearing in mind that such a relatively simple reaction unexpectedly demonstrated a number of structurally different products, one can anticipate a variety of interesting architectures based on $[Re_{12}CS_{17}(CN)_6]^{6-}$, remaining to be discovered for other transition and post-transition metals.

## Supplementary material

Crystallographic data for the structure of the title compound reported in this article has been deposited at the Cambridge Crystallographic Data Center, CCDC 825759. These data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge

CB2 1EZ, UK; Fax: (+44) 1223-336-033; http://www.ccdc.cam.ac.uk/conts/retrieving.html.

## Acknowledgments

This work was supported by the Russian Foundation for Basic Research (project No. 10-03-01040) and by the State Contract No. 02.740.11.0628.

## References

[1] L.G. Beauvais, M.P. Shores, J.R. Long. *Chem. Mater.*, **10**, 3783 (1998).
[2] M.P. Shores, L.G. Beauvais, J.R. Long. *Inorg. Chem.*, **38**, 1648 (1999).
[3] M.V. Bennett, M.P. Shores, L.G. Beauvais, J.R. Long. *J. Am. Chem. Soc.*, **122**, 6664 (2000).
[4] M.V. Bennett, L.G. Beauvais, M.P. Shores, J.R. Long. *J. Am. Chem. Soc.*, **123**, 8022 (2001).
[5] K.A. Brylev, Y.V. Mironov, N.G. Naumov, V.E. Fedorov, J.A. Ibers. *Inorg. Chem.*, **43**, 4833 (2004).
[6] N.G. Naumov, A.V. Virovets, S.B. Artemkina, D. Yu. Naumov, J.A.K. Howard, V.E. Fedorov. *J. Solid State Chem.*, **177**, 1896 (2004).
[7] O.A. Efremova, Y.V. Mironov, N.V. Kuratieva, V.E. Fedorov. *Russ. J. Coord. Chem.*, **32**, 483 (2006).
[8] K.A. Brylev, G. Pilet, N.G. Naumov, A. Perrin, V.E. Fedorov. *Eur. J. Inorg. Chem.*, 461 (2005).
[9] O.A. Efremova, Y.V. Mironov, V.E. Fedorov. *Eur. J. Inorg. Chem.*, 2533 (2006).
[10] N.G. Naumov, A.V. Virovets, V.E. Fedorov. *Inorg. Chem. Commun.*, **3**, 71 (2000).
[11] Y. Kim, S.-M. Park, S.-J. Kim. *Inorg. Chem. Commun.*, **5**, 592 (2002).
[12] S. Kim, Y. Kim, J. Lee, W. Shin, M. Lee, S.-J. Kim. *Inorg. Chim. Acta*, **360**, 1890 (2007).
[13] Y. Kim, S. Kim, S.-J. Kim, M.K. Lee, M. Kim, H. Lee, C.S. Chin. *Chem. Commun.*, 1692 (2004).
[14] Y.V. Mironov, N.G. Naumov, K.A. Brylev, O.A. Efremova, V.E. Fedorov, K. Hegetschweiler. *Angew. Chem. Int. Ed.*, **43**, 1297 (2004).
[15] Y.V. Mironov, N.G. Naumov, S.G. Kozlova, S.-J. Kim, V.E. Fedorov. *Angew. Chem. Int. Ed.*, **44**, 6867 (2005).
[16] S.P. Gabuda, S.G. Kozlova, Y.V. Mironov, V.E. Fedorov. *Nanoscale Res. Lett.*, **4**, 1110 (2009).
[17] Y.V. Mironov, N.G. Naumov, S-J. Kim, V.E. Fedorov. *Russ. J. Coord. Chem.*, **33**, 279 (2007).
[18] Y.V. Mironov, S-J. Kim, V.E. Fedorov. *Russ. Chem. Bull.*, **57**, 2271 (2008).
[19] Bruker AXS Inc. *APEX2* (Version 1.08), *SAINT* (Version 7.03), *SADABS* (Version 2.11). Madison, Wisconsin, USA (2004).
[20] G.M. Sheldrick. *Acta Crystallogr.*, **A64**, 112 (2008).
[21] K.A. Brylev, N.G. Naumov, G. Peris, R. Llusar, V.E. Fedorov. *Polyhedron*, **22**, 3383 (2003).
[22] Y.V. Mironov, O. Oeckler, A. Simon, V.E. Fedorov. *Eur. J. Inorg. Chem.*, 2751 (2001).
[23] O.A. Efremova, Y.V. Mironov, N.V. Kuratieva, V.E. Fedorov. *Russ. Chem. Bull.*, **55**, 1946 (2006).
[24] Y.V. Mironov, N.G. Naumov, K.A. Brylev, O.A. Efremova, V.E. Fedorov, K. Hegetschweiler. *Russ. J. Coord. Chem.*, **31**, 269 (2005).
[25] Y.V. Mironov, O.A. Efremova, D.Y. Naumov, W.S. Sheldrick, V.E. Fedorov. *Eur. J. Inorg. Chem.*, 2591 (2003).
[26] Y.V. Mironov, V.E. Fedorov, I. Ijjaali, J.A. Ibers. *Inorg. Chem.*, **40**, 6320 (2001).
[27] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, John Wiley & Sons Inc., New York (1997).