

Two Molecular-Type Complexes of the Octahedral Rhenium(III) Cyanocluster Anion $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ with M^{2+} (Mn^{2+} , Ni^{2+})

Sofia B. Artemkina,^[a] Nikolai G. Naumov,^{*[a]} Alexander V. Virovets,^[a] Oliver Oeckler,^[b] Arndt Simon,^[b] Simon B. Erenburg,^[a] Nikolai V. Bausk,^[a] and Vladimir E. Fedorov^[a]

Keywords: Rhenium / Cluster compounds / Structure elucidation / Cyanide ligands / XANES

Two novel octahedral rhenium(III) selenocyanide cluster complexes $[(n\text{Bu})_4\text{N}]_2\text{Ni}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**1**) and $[(n\text{Bu})_4\text{N}]_2\text{Mn}(\text{H}_2\text{O})_4[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**2**) have been prepared by the reaction of $\text{K}_4[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 3.5\text{H}_2\text{O}$, $(n\text{Bu})_4\text{NBr}$ and $\text{Ni}(\text{OAc})_2$ (or MnSO_4) in aqueous solution. The complexes have been structurally solved in the orthorhombic unit cell *Pbca* with parameters: $a = 19.393(2)$, $b = 17.292(2)$, $c = 37.255(4)$ Å for **1**, and $a = 19.518(4)$, $b = 17.488(3)$, $c = 37.997(5)$ Å for **2**. The cluster anions and M^{2+} form ionic pairs

$\{\text{M}(\text{H}_2\text{O})_n[\text{Re}_6\text{Se}_8(\text{CN})_6]\}^{2-}$ that are packed in the solid state with *n*-tetrabutylammonium cations. Coordinated and solvate water molecules as well as the nitrogen atoms of the anions form a network of hydrogen bonds in the structures. These compounds are isomorphous, although the coordination environments of the metal cations differ.

(© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

Introduction

The ability of CN ligands to form strong covalent bonds to 3d transition metals is well-known and the coordination chemistry of mononuclear cyanometallates is well developed.^[1] Complex cluster anions $[\text{Re}_6(\mu_3\text{-Se})_8(\text{CN})_6]^{4-}$ with terminal CN groups^[2] can also interact with transition metals to form new polymeric cluster solids based on -Re-C≡N-M-N≡C-Re- bridges.^[3,4] The type of polymeric compound formed and the coordination environment of the metal cation are influenced enormously by the nature of the additional cations present in the reaction mixture. We have found that an increase of cation size in the series $\text{Cs}^+ < \text{Me}_4\text{N}^+ < \text{Et}_4\text{N}^+ < n\text{Pr}_4\text{N}^+$ results in a reduction of the dimensionality of the formed solids. In the case of Cs^+ ,^[3a] Me_4N^+ and Et_4N^+ ,^[3b] a three-dimensional polymeric framework $\{\text{M}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2\}^{2-}$ is formed which includes these cations and water molecules in its cavities. In the case of $n\text{Pr}_4\text{N}^+$,^[3c] polymeric chains or molecular-type structures built from complex anions and M^{2+} are obtained.

Here we report the synthesis and structures of two novel isomorphous complexes $(n\text{Bu}_4\text{N})_2\text{Ni}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**1**) and $(n\text{Bu}_4\text{N})_2\text{Mn}(\text{H}_2\text{O})_4[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**2**) obtained from the reaction of aqueous solutions of $\text{K}_4\text{Re}_6\text{Se}_8(\text{CN})_6$ and M^{2+} (Mn^{2+} and Ni^{2+}) in

the presence of Bu_4NBr . Although the space group, cell parameters and packing motifs in these structures are similar, the coordination spheres of Mn^{2+} and Ni^{2+} are quite different.

Results and Discussion

Structures of Compounds 1 and 2

The anion $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ has the usual $\text{Re}_6\text{X}_8\text{L}_6$ environment (Figure 1). Six rhenium atoms form an Re_6 octahedron with the faces μ_3 -capped by eight selenium atoms. The CN ligands are coordinated to rhenium atoms through the carbon atom. The bond lengths and angles in the anion (see Table 1) do not differ from those found in other salts with an Re_6Se_8 cluster core $[\text{K}_4\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 3.5\text{H}_2\text{O}$:^[2] $\text{Re-Re} = 2.633$ Å; $\text{Re-Se} = 2.526$ Å; $\text{Re-C} = 2.11$ Å; $\text{C-N} = 1.15$ Å; $\text{NaCs}_3\text{Re}_6\text{Se}_8(\text{CN})_6$:^[4] $\text{Re-Re} = 2.634$ Å; $\text{Re-Se} = 2.52$ Å; $\text{Re-C} = 2.10$ Å; $\text{C-N} = 1.17$ Å; $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$:^[5] $\text{Re-Re} = 2.625$; $\text{Re-Se} = 2.519$ Å].

The cluster anion forms bridging Re-CN-M contacts at one nitrogen atom, with the other five CN groups remaining terminal, therefore we have an ionic pair containing an M^{2+} cation. The structures of the ionic pairs $\{\text{M}(\text{H}_2\text{O})_n[\text{Re}_6\text{Se}_8(\text{CN})_6]\}^{2-}$ for **1** and **2** are shown in Figure 2, with water molecules completing the coordination sphere of M^{2+} .

In compound **1** the coordination environment of Ni^{2+} is a slightly distorted octahedron ($\text{N} + 5\text{O}$), with Ni-N distances of 2.032(7) Å and Ni-O distances ranging from 2.033(6) to 2.118(7) Å. The hydrogen bond system can be

^[a] Institute of Inorganic Chemistry SB RAS, 3, Ak. Lavrentiev Ave., 630090 Novosibirsk, Russia
Fax: (internat.) + 7-3832/344-489
E-mail: naumov@che.nsk.su

^[b] Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

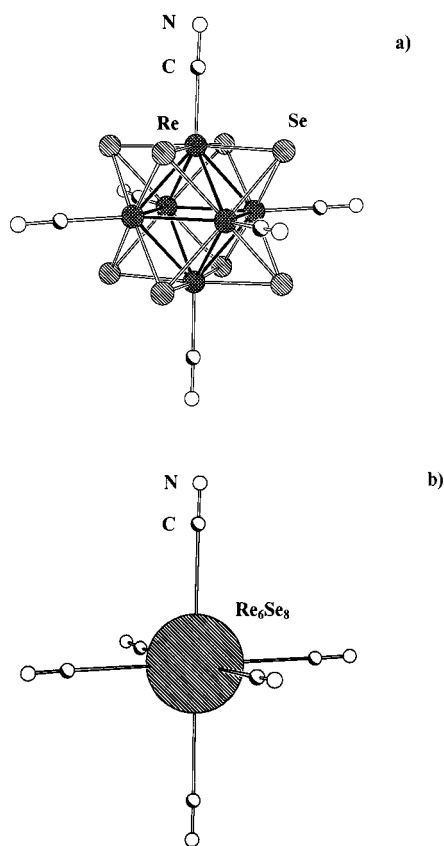


Figure 1. Structure of cluster anion $[\text{Re}_6(\mu_3\text{-Se})_8(\text{CN})_6]^{4-}$ (a) and its simplified presentation (b)

described as a superposition of two chains running along the c and a axes. The first of them consists of water molecules, O1 and O1w, and the terminal nitrogen atom N2 from the nickel-cluster ionic pair. The second includes O5, O2w and N6. The $\text{O}\cdots\text{N}$ and $\text{O}\cdots\text{O}$ distances are about 2.6–2.7 Å (Figure 3a).

In **2** the Mn^{2+} ion is coordinated by the nitrogen atom of the cluster anion and by four (rather than five) water molecules, with $\text{Mn}-\text{O}$ distances ranging between 2.13(2) and 2.15(2) Å. Thus the coordination environment of Mn^{2+} is $\text{N} + 4\text{O}$ and the coordination polyhedron is a distorted square pyramid (reversed umbrella) with an apex at the nitrogen atom. The manganese atom lies 0.55 Å out of the plane formed by the atoms O1, O2, O3, and O4. The next nearest water molecule, O1w, lies 3.65 Å from Mn1 (Figure 3b), forming a hydrogen bond with O3 ($\text{O}\cdots\text{O}$ distance of 2.70 Å). As in **1**, there are hydrogen bonded chains running roughly along c axis.

In the related compound $[(n\text{Pr})_4\text{N}]_2\text{Mn}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot\text{H}_2\text{O}$ (**3**), the environment of Mn^{2+} is different.^[3c] An $\{\text{Mn}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\}$ fragment of **3** is shown in Figure 2c and some bond lengths and angles are presented in Table 2 for comparison. In contrast to compounds **1** and **2**, the manganese(II) cation in **3** has a distorted octahedral coordination environment $[\text{1N} + 5\text{O}(\text{H}_2\text{O})]$ with an $\text{Mn}-\text{N}-\text{C}$ angle of $158(5)^\circ$. The reason for such a deviation from linearity is the different arrangement of the ionic pairs in the solid state. In **1** and **2** the ionic pairs are oriented along the c axis of the unit cell (Figure 3a and 3b) and have an arrangement similar to that in compound **3**.^[3c] As in **3**, the cluster anions form a pseudo face-centred motif. In **1**

Table 1. Crystallographic data for compounds $(\text{Bu}_4\text{N})_2\text{Ni}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**1**) and $(\text{Bu}_4\text{N})_2\text{Mn}(\text{H}_2\text{O})_4[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**2**)

	1	2
Empirical formula	$\text{C}_{38}\text{H}_{86}\text{N}_8\text{NiO}_7\text{Re}_6\text{Se}_8$	$\text{C}_{38}\text{H}_{84}\text{MnN}_8\text{O}_6\text{Re}_6\text{Se}_8$
Molecular weight	2574.74	2552.95
Colour, habit	yellow, irregular polyhedron	red, octahedral
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>
a (Å)	19.393(2)	19.518(4)
b (Å)	17.292(2)	17.488(3)
c (Å)	37.255(4)	37.997(5)
Z	8	8
Cell volume (Å ³)	12493(2)	12970(4)
Exp. hkl limits	$-25 \leq h \leq 25$ $-22 \leq k \leq 22$ $-48 \leq l \leq 48$	$0 \leq h \leq 23$ $0 \leq k \leq 20$ $0 \leq l \leq 45$
Calcd. density (g·cm ⁻³)	2.738	2.615
Absorption correction	multi-scan	4 azimuthal scan curves
Absorption coefficient (mm ⁻¹)	16.580	15.87
Diffractometer type	Stoe IPDS	Enraf–Nonius CAD4 with graphite monochromator
Crystal size (mm)	$0.214 \times 0.243 \times 0.257$	$0.6 \times 0.4 \times 0.2$
$2\theta_{\text{max}}$ (°)	55	50
Reflections collected/unique	14338/11216 [$R(\text{int}) = 0.0672$]	7439/7118 [all unique]
Final R indices for all $F_o > 4\sigma(F_o)$	$R1 = 0.0372$; $wR2 = 0.0819$	$R1 = 0.033$; $wR2 = 0.068$
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.0457P)^2 + 25.00P$ where $P = (F_o^2 + 2F_c^2)/3$	$w^{-1} = \sigma^2(F_o^2) + (0.0128P)^2$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
Max., min. peak in final diff. map (e·Å ⁻³)	2.537, -2.180	-1.00, 0.88

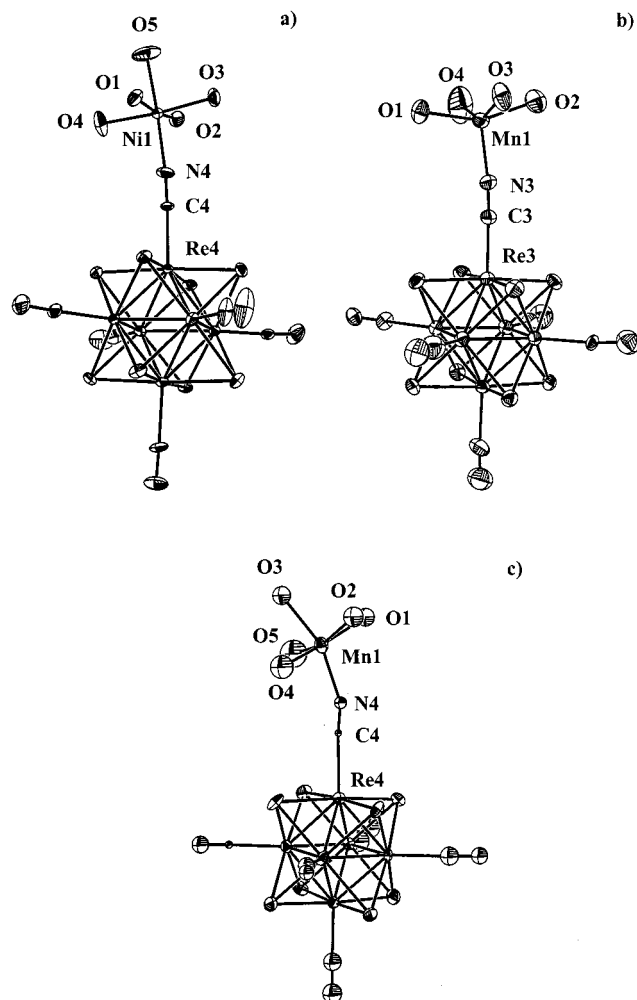


Figure 2. Structures of anionic pairs in compounds **1** (a), **2** (b) and **3** (c); thermal ellipsoids are drawn at a 50% probability level

the ionic pairs are connected by hydrogen bonds to the solvent water molecule O2w. The nickel atom has an almost regular octahedral environment and both the O5 and O2w water molecules form hydrogen bonds with normal distances (O5...O2w: 2.65 Å; O2w...N6: 2.76 Å) and angles (N6...O2w...O5: 131°). In **3** the ionic pairs interact directly through the O3...N2 hydrogen bond. This interaction forces a deviation of the C4–N4–Mn1 (158°) and N4–Mn1–O3 (159°) angles from linearity, thus allowing the O3 atom to form a normal hydrogen bond to N2 with an O–N distance of 2.77 Å and an Mn1–O3–N2 angle of 116°.

The space between the ionic pairs is occupied by Bu₄N⁺ cations. Two crystallographically independent Bu₄N⁺ cations have different conformations in the structure.

Although the coordination number of five for Mn²⁺ is known in the literature this environment is not usual for manganese and is mainly caused by steric factors, namely the volume of the organic ligands. Stelzig et al.^[6] have reported the complexes [Mn^{II}L³(μ₃-OMe)(MeOH)]₂ and Na[Mn^{III}(L³)₂(μ₂-OAc)]·H₂O·0.25THF, where L³ = 1,5-bis(3-Cl, 5-NO₂-salicylideneamino)pentan-3-ol, a voluminous pentadentate ligand. The Mn²⁺ coordination arrange-

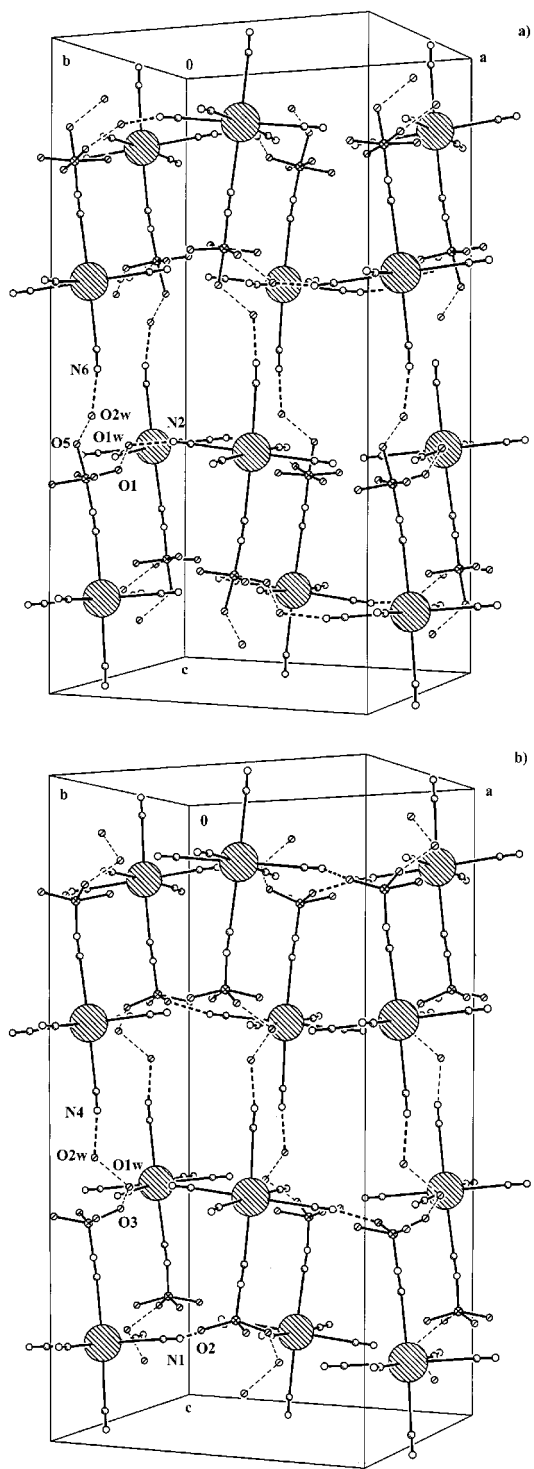


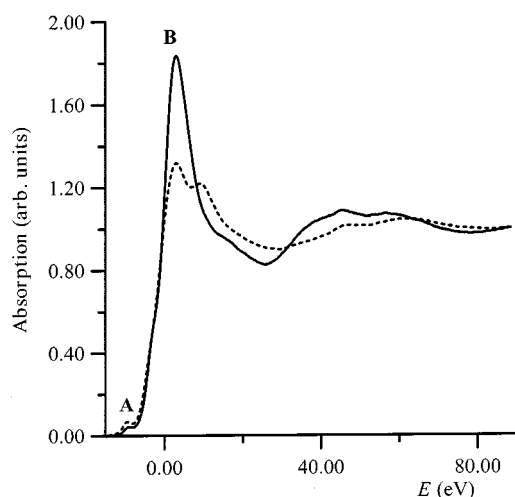
Figure 3. Packing motifs of ionic pairs for compounds **1** (a) and **2** (b); *n*Bu₄N⁺ cations are omitted for clarity; large hatched circles represent the {Re₆Se₈} cores of the cluster anions

ment here is 4O + N. It is also worthwhile to note the complex [Mn₃(L¹O)₄(MeCN)][ClO₄]₂·H₂O, where L¹O is a deprotonated tridentate ligand (2-hydroxyphenyl)bis(pyrazolyl)methane.^[7]

To confirm the difference in the manganese environments in **2** and **3** we have recorded the MnK XANES (X-ray Absorption Near Edge Structure) spectra for these com-

Table 2. Selected bond lengths and angles for compounds $(\text{Bu}_4\text{N})_2\text{Ni}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**1**), $(\text{Bu}_4\text{N})_2\text{Mn}(\text{H}_2\text{O})_4[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (**2**), and $(\text{Pr}_4\text{N})_2\text{Mn}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot \text{H}_2\text{O}$ (**3**) (Min. Max.; Mean)

	1	2	3
Bond lengths (Å)			
Re–Re	2.6182(4)–2.6372(4); 2.6262	2.6171(17)–2.6371(16); 2.630	2.609(5)–2.647(5); 2.629
Re–Se	2.4937(7)–2.5180(8); 2.5095	2.498(4)–2.528(4); 2.517	2.49(1)–2.54(1); 2.51
Re–C	2.070(7)–2.109(7); 2.093	2.05(3)–2.23(3); 2.11	2.14(6)–2.31(3); 2.20
M–N	2.032(7)	2.099(19)	2.08(4)
M–O	2.033(6)–2.118(7); 2.065	2.13(2)–2.15(2); 2.14	2.14(6)–2.24(4); 2.19
C–N	1.144(11)–1.157(10); 1.149	1.11(3)–1.22(3); 1.17	1.03(4)–1.24(8); 1.11
Bond angles (°)			
N–M–O	92.6(3)–95.0(3); 93.4	102.4(8)–110.9(10); 105.1	83(2)–106(2); 95
N–M–O (trans)	176.0(3)	–	159(2)
O–M–O	83.0(3)–91.0(3); 88.2	84.7(7)–87.9(7); 86.4	79(2)–109(2); 88
O–M–O (trans)	171.6(2), 174.9(3); 173.3	144.8(9), 154.7(7); 149.8	161(2)–168(2); 165
Re–C–N (terminal)	176.6(7)–179.2(8); 177.9	171.2(3)–178.7(3); 174.6	142.4(7)–177.9(6); 165.6
Re–C–N (bridging)	177.2(7)	176(3)	174(5)
M–N–C	174.9(6)	174(2)	158(5)

Figure 4. Mn-K XANES spectra of compounds **2** (dashed line) and **3** (solid line)

pounds (Figure 4). The maximum B in the spectra of **2** and **3** (Figure 4) corresponds to an electron transition from the $\text{Mn}1s$ to the $\text{Mn}4p$ level. The decrease of intensity of this maximum by a factor of two for compound **2** relative to compound **3** can clearly be seen. This decrease indicates a splitting of the $4p$ electronic levels due to substantially reduced symmetry for the first sphere of the Mn environment in **2**.^[12] The pre-edge resonance (maximum A) corresponding to the quadrupole $\text{Mn}1s\text{--Mn}3d$ transition (Figure 4) is sensible to symmetry distortion at the manganese atom. A noticeable increase of the intensity in **2** relative to **3** also indicates a symmetry lowering of the Mn environment in the former compound. These results are in accordance with the X-ray structural data for compounds **2** and **3**.

Experimental Section

Physical Measurements: Elemental analyses for C, H, N, S (Carlo Erba 1106) were performed in the Laboratory of Microanalysis of

the Institute of Organic Chemistry, Novosibirsk. Infrared spectra were measured on KBr disks with a Bruker IFS-85 Fourier spectrometer. For determination of water the curves of mass losses and TGD curves of the compounds were recorded at a heating rate of $3^\circ\text{C}/\text{min}$ (temperature range $20\text{--}300^\circ\text{C}$) under an atmosphere of argon with a TGD-7000 RH thermal analysis controller (Sinku-Riku, Japan). Measurement of Mn-K XANES spectra were performed using synchrotron radiation of the VEPP-3 storage ring at the Budker Institute of Nuclear Physics at Novosibirsk. A channel-cut Si (111) single crystal was used as the two-crystal monochromator. The spectra were obtained using the transmission mode.

X-ray Structural Measurements: The structures of **1** and **2** were determined by X-ray structural analysis. Crystallographic data and details of diffraction measurements are given in Table 1. Both structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 .

Structural Studies of $[(n\text{Bu})_4\text{N}]_2\text{Ni}(\text{H}_2\text{O})_5[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (1**):** The diffraction data were collected with a Stoe IPDS diffractometer with graphite-monochromated Mo-K_α radiation at $T = 93(2)\text{ K}$ using the ϕ -oscillation method. Absorption correction were applied using information from multiple scans. Anisotropic displacement parameters were refined for all non-H atoms. The final difference electron density map features were with no chemical meaning. Experimental crystal data are listed in Table 1. The calculations were performed with SHELX-97^[8] and standard Stoe IPDS software.^[9]

Structural Studies of $[(n\text{Bu})_4\text{N}]_2\text{Mn}(\text{H}_2\text{O})_4[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ (2**):** The diffraction data were collected with an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation at ambient conditions ($T = 291\text{ K}$). Reflection intensities were collected by standard techniques [$\theta/2\theta$ scans with variable speed, ω range ($^\circ$) = $0.9 + 0.35\text{tg}(\theta)$] and absorption corrections were applied by measuring azimuthal scan curves. Anisotropic displacement parameters were refined for all non-H atoms. The final difference electron density map features were with no chemical meaning. The calculations were performed with the standard Enraf–Nonius CAD4 programs (CD4CA0, CADDAT) and SHELX-93 (structure solution and refinement).^[10]

Syntheses: The starting cluster compound $\text{K}_4[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 3.5\text{H}_2\text{O}$ was prepared from polymeric $\text{Re}_6\text{Se}_8\text{Br}_2$ ^[11] as described in refs.^[2] All other reagents were employed as purchased.

[(*n*Bu)₄N]₂Ni(H₂O)₅[Re₆Se₈(CN)₆]·2H₂O (1): A mixture of (*n*Bu)₄NBr (160 mg, 0.48 mmol) and Ni(OAc)₂·4H₂O (60 mg, 0.24 mmol) in 20 mL of water was gradually added to a hot solution of K₄Re₆Se₈(CN)₆·3.5H₂O (500 mg, 0.24 mmol) in 10 mL of water. The resulting mixture was stirred and heated for two hours. The fine orange precipitate was then washed with water (3 × 15 mL) and dried. Yield: quantitative (605 mg, 98%); C₃₈H₈₆N₈NiO₇Re₆Se₈ (2574.74): calcd. C 17.85, H 3.31, N 4.38; found C 18.10, H 3.46, N 4.49. Mass loss 4.4% at 105 °C (calcd 4.2% for six water molecules). IR: $\tilde{\nu}$ = 2109 (intense), 2142 (shoulder) (CN); 1620 cm⁻¹ (weak) (H₂O).

[(*n*Bu)₄N]₂Mn(H₂O)₄[Re₆Se₈(CN)₆]·2H₂O (2): A mixture of (*n*Bu)₄NBr (160 mg, 0.48 mmol) and MnSO₄·5H₂O (240 mg, 1 mmol) in 20 mL of water was gradually added to a hot solution of K₄Re₆Se₈(CN)₆·3.5H₂O (500 mg, 0.24 mmol) in 10 mL of water. The resulting mixture was stirred and heating for two hours. The fine orange precipitate was then washed with water (3 × 15 mL) and dried. Yield: quantitative (582 mg, 95%); C₃₈H₈₄MnN₈O₆Re₆Se₈ (2552.95): calcd. C 17.88, H 3.32, N 4.39; found C 18.00, H 3.49, N 4.45. IR: $\tilde{\nu}$ = 2108 (intense), 2130 (shoulder) (CN); 1649 cm⁻¹ (weak) (H₂O).

Single Crystal Growth: Both compounds have low solubility and therefore crystals suitable for X-ray single crystal analysis were grown in a U-tube filled with silica gel as described in ref.^[3a] The crystals were located near the middle part of the U-tube. The following reagents were used: K₄Re₆Se₈(CN)₆·3.5H₂O, *n*Bu₄NBr, Ni(OAc)₂·4H₂O for **1**, Mn(OAc)₂·4H₂O for **2**. Octahedral red crystals can be easily separated from the silica gel manually. X-ray powder diffraction and IR spectroscopy confirmed the identity of these crystals.

CCDC-167585 (**1**) and CCDC-167586 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-0033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by Russian Foundation for Basic Research, grant nos. 99-03-32789 and 99-03-33301. Authors thank the

Program for Support of Young Scientists of the Siberian Branch of the Russian Academy of Sciences for financial support.

- [1] K. R. Dunbar, R. A. Heintz, in *Progress in Inorg. Chem.* (Ed.: K. D. Karlin) **1997**, 45, 283–391. T. Iwamoto, in *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. Macnicol, F. Vögtle), Pergamon **1996**, 6, 643–690. B. H. Chadwick, A. G. Sharpe, *Advances in Inorganic and Radiochemistry* (Eds.: H. J. Emeleus, A. G. Sharpe), Academic Press, New York **1996**, 8, 83–177.
- [2] N. G. Naumov, A. V. Virovets, N. V. Podberezhskaya, V. E. Fedorov, *Russ. J. Struct. Chem.* **1997**, 38, 857–862. H. Imoto, N. G. Naumov, A. V. Virovets, T. Saito, V. E. Fedorov, *Russ. J. Struct. Chem.* **1997**, 39, 720–727. Yu. V. Mironov, J. A. Cody, T. E. Albrecht-Schmitt, J. A. Ibers, *J. Am. Chem. Soc.* **1997**, 119, 493–498.
- [3] [3a] N. G. Naumov, A. V. Virovets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem. Int. Ed.* **1998**, 37, 1943–1945. [3b] N. G. Naumov, A. V. Virovets, V. E. Fedorov, *Russ. J. Struct. Chem.* **2000**, 41, 499–520. [3c] N. G. Naumov, S. B. Artemkina, A. V. Virovets, V. E. Fedorov, *J. Solid State Chem.* **2000**, 153, 195–204. [3d] N. G. Naumov, A. V. Virovets, Yu. V. Mironov, S. B. Artemkina, V. E. Fedorov, *Ukr. Khim. Zh.* **1999**, 65, 21–27.
- [4] L. G. Beauvais, M. P. Shores, J. R. Long, *Chem. Mater.* **1998**, 10, 3783–3786. M. P. Shores, L. G. Beauvais, J. R. Long, *Inorg. Chem.* **1999**, 38, 1648–1649. L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, 122, 2763–2772.
- [5] J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, 118, 4603–4616.
- [6] L. Stelzig, A. Steiner, B. Chansou, J. P. Tuchagues, *Chem. Commun.* **1998**, 7, 771–772.
- [7] T. C. Higgins, K. Spartalian, C. J. O'Connor, B. F. Matzkanke, C. J. Carrano, *Inorg. Chem.* **1998**, 37, 2263–2272.
- [8] G. M. Sheldrick, SHELX-97, Release 97-2, University of Goettingen, Germany, **1998**.
- [9] Stoe IPDS software, Darmstadt **1998**.
- [10] G. M. Sheldrick, **1993**, *Acta Crystallogr. A49 (Suppl.)*, p. C53.
- [11] A. Perrin, L. Leduc, M. Sergent, *Eur. J. Solid State Chem.* **1991**, 28, 919–931.
- [12] [12a] F. W. Lytle, R. B. Gregor, A. J. Panson, *Phys. Rev. B* **1988**, 37, 1550–1562. [12b] H. T. Tsang, J. E. Penner-Hahn, C. J. Batie, *Physica B* **1989**, 158, 115–116. [12c] R. A. Scott, *Physica B* **1989**, 158, 84–86.

Received September 9, 2001
[101349]