

# PSEUDOHEXAGONAL MOTIF OF THE ARRANGEMENT OF COMPLEX ANIONS IN THE STRUCTURE OF $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$

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The  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  salt was obtained; its crystal structure was analyzed:  $a = 10.7713(9)$  Å,  $b = 13.9602(11)$  Å,  $c = 14.7956(11)$  Å,  $\alpha = 91.961(3)^\circ$ ,  $\beta = 109.985(3)^\circ$ ,  $\gamma = 110.030(3)^\circ$ ,  $V = 1935.3(3)$  Å<sup>3</sup>, space group  $P\bar{1}$ ,  $Z = 2$ ,  $d_{\text{calc}} = 3.441$  g/cm<sup>3</sup>. In the cluster anion, the Re–Re distances lie in the range from 2.594 Å to 2.612 Å. For two crystallographically independent complex cations, Ru–N<sub>av</sub> is 2.105 Å, and Ru–Cl<sub>av</sub> 2.329 Å. A pseudo-hexagonal motif of the structure was found.

**Keywords:** X-ray diffraction analysis, X-ray phase analysis, ruthenium, rhenium, crystal chemistry, chloropentammine.

Active studies are under way to find new functional materials based on rhenium clusters of different compositions and structures. The structures of these compounds can be insular (built of isolated neutral or charged particles), chained, layered, or built of networks. In the literature, reviews are available on the crystal chemistry of compounds containing the  $[\text{Re}_6\text{X}_8(\text{CN})_6]^{4-}$  octahedral anion ( $\text{X} = \text{S}, \text{Se}, \text{Te}$ ) and various cations [1, 2]. However, there are few examples of the formation of compounds involving isolated cations and anions, for instance [3, 4]. The effect of cations on the structure of an isolated cluster anion can be revealed more completely if these salts are obtained.

The aim of this work was synthesis and analysis of the crystal structure of the  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  salt containing a rather inert isolated  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$  cation.

**Experimental.**  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  was synthesized as follows.  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (0.026 g, 0.09 mmol) was dissolved in hot water (10 ml) and mixed with a solution of  $\text{Cs}_3\text{K}[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$  (0.100 g, 0.05 mmol) in hot water (10 ml). After a day, the solution yielded dark-red needle crystals of the salt. The yield was 66% as calculated for the introduced ruthenium. The IR spectrum was recorded (Scimitar FTS 2000, KBr pellet) in a range from 400 cm<sup>–1</sup> to 4000 cm<sup>–1</sup>: 3433s, ( $\nu\text{H}_2\text{O}$ ), 3236s, 3172s ( $\nu\text{NH}_3$ ), 2113s ( $\nu\text{CN}$ ), 1613m ( $\delta_{\text{d}}\text{HNN} + \delta_{\text{d}}\text{HOH}$ ), 1305w ( $\delta_{\text{s}}\text{HNN}$ ), 719w ( $\rho_{\text{r}}\text{NH}_3$ ), 403w ( $\nu\text{RuN}$ ). An X-ray phase analysis (DRON-3M,  $\text{CuK}\alpha$  radiation), performed on single crystal data, showed that the product was monophasic.

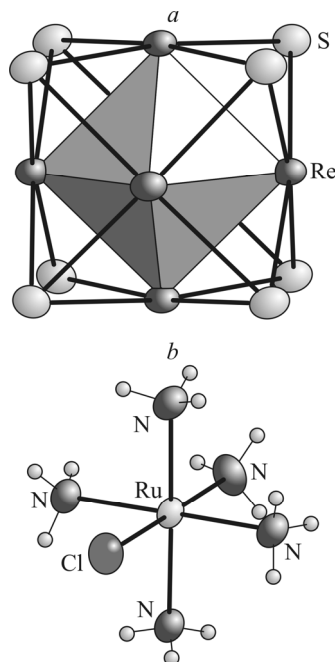
Crystals for an X-ray diffraction analysis were selected from the bulk. All the crystals examined were highly perfect. The unit cell parameters were refined and the intensity of diffraction reflections measured on a Bruker X8 APEX diffractometer ( $\text{MoK}\alpha$  radiation, graphite monochromator, CCD detector,  $\theta$  range from 1.49° to 31.62°, 22451 reflections measured, room temperature). The completeness of data collection was 99.3% for  $\theta = 25.00^\circ$ . The structure was solved by the

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**TABLE 1.** Bond Lengths  $d$  (Å) for  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ 

Bond	$d$	Bond	$d$
Anion 1		Anion 2	
Re(1)–Re(5)	2.5937(4)	Re(2)–Re(6)#2	2.5998(4)
Re(1)–Re(3)	2.5937(4)	Re(2)–Re(4)	2.6045(5)
Re(1)–Re(3)#1	2.6113(4)	Re(2)–Re(4)#2	2.6102(5)
Re(1)–Re(5)#1	2.6117(4)	Re(2)–Re(6)	2.6104(4)
Re(3)–Re(5)	2.5980(4)	Re(4)–Re(6)#2	2.6024(5)
Re(3)–Re(5)#1	2.5991(4)	Re(4)–Re(6)	2.6027(5)
Average	<b>2.6013</b>	Average	<b>2.6050</b>
Re(1)–S(14)	2.403(2)	Re(2)–S(12)#2	2.401(2)
Re(1)–S(13)#1	2.408(2)	Re(2)–S(11)	2.404(2)
Re(1)#1–S(13)	2.4076(19)	Re(2)–S(5)	2.416(2)
Re(1)–S(10)	2.4127(19)	Re(2)–S(6)	2.418(2)
Re(1)–S(9)	2.4135(19)	Re(4)–S(5)	2.397(2)
Re(3)–S(10)	2.4037(18)	Re(4)–S(12)	2.405(2)
Re(3)–S(14)	2.4073(19)	Re(4)–S(11)	2.414(2)
Re(3)–S(9)#1	2.4093(19)	Re(4)–S(6)#2	2.416(2)
Re(3)–S(13)	2.4123(18)	S(11)–Re(6)	2.408(2)
Re(5)–S(9)	2.4146(19)	S(12)–Re(2)#2	2.401(2)
Re(5)–S(13)	2.4242(19)	S(12)–Re(6)	2.410(2)
Re(5)–S(14)	2.4123(19)	Re(6)–S(5)#2	2.405(2)
Re(5)–S(10)#1	2.3986(19)	Re(6)–S(6)	2.419(2)
Average	<b>2.410</b>	Average	<b>2.409</b>
Re(1)–C(3)	2.107(8)	Re(2)–C(9)	2.126(8)
Re(3)–C(4)	2.111(8)	Re(4)–C(19)	2.115(8)
Re(5)–C(8)	2.118(8)	Re(6)–C(11)	2.131(8)
Average	<b>2.112</b>	Average	<b>2.124</b>
C(3)–N(6)	1.157(11)	C(9)–N(18)	1.135(10)
C(8)–N(7)	1.134(11)	C(11)–N(13)	1.133(11)
C(4)–N(8)	1.123(11)	C(19)–N(11)	1.152(11)
Average	<b>1.138</b>	Average	<b>1.140</b>
Cation 1		Cation 2	
Ru(1)–N(5)	2.087(8)	Ru(2)–N(14)	2.073(9)
Ru(1)–N(10)	2.088(7)	Ru(2)–N(3)	2.095(7)
Ru(1)–N(4)	2.100(7)	Ru(2)–N(2)	2.097(7)
Ru(1)–N(9)	2.118(7)	Ru(2)–N(1)	2.110(8)
Ru(1)–N(17)	2.154(8)	Ru(2)–N(12)	2.123(8)
Average	<b>2.109</b>	Average	<b>2.100</b>
Ru(1)–Cl(2)	2.338(2)	Ru(2)–Cl(1)	2.320(3)

standard heavy metal method and refined in the anisotropic approximation, and all calculations were carried out with SHELX-97 software [5]. The analyzed structure was isostructural with  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  and  $[\text{Ir}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  [6, 7]. The final refinement of the crystal structure was performed in a full-matrix approximation over 10,435 independent reflections;  $R1 = 0.0424$  ( $wR2 = 0.0954$ ). For 9055 reflections with  $I > 2\sigma(I)$ ,  $R1 = 0.0355$  ( $wR2 = 0.0923$ ). The  $S$  factor was 1.033 on  $F^2$ . The crystal data for  $\text{C}_6\text{H}_{30}\text{Cl}_2\text{N}_{16}\text{O}_2\text{Re}_6\text{Ru}_2\text{S}_8$ :  $a = 10.7713(9)$  Å,  $b = 13.9602(11)$  Å,  $c = 14.7956(11)$  Å,  $\alpha = 91.961(3)^\circ$ ,  $\beta = 109.985(3)^\circ$ ,  $\gamma = 110.030(3)^\circ$ ,  $V = 1935.3(3)$  Å<sup>3</sup>, space group  $P\bar{1}$ ,



**Fig. 1.** Structure of ions in the crystal structure of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ : (a)  $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$  anions (CN groups not shown), (b)  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$  complex cation.

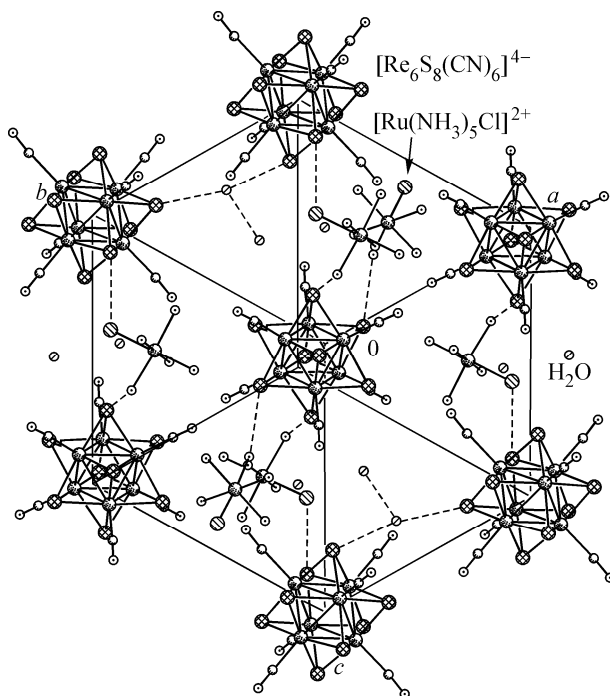
$Z = 2$ , molecular weight 2005.18,  $d_{\text{calc}} = 3.441 \text{ g/cm}^3$ . The atomic coordinates and thermal parameters were deposited in the ICSD (Inorganic Crystal Structure Database) [8]. The bond lengths are given in Table 1.

**Crystal structure description.** The crystal structure is built of isolated  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$  cations,  $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$  sulfocyanide cluster anions, and crystallization water molecules. Figure 1 depicts the structure of the complex ions. The geometric characteristics of two crystallographically independent complex anions (Table 1) almost coincide. The Re–Re distances vary from 2.5937(4) Å to 2.6117(4) Å in these anions, the lower limit being slightly smaller than in the known sulfocyanide cluster anions,  $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ . Thus, the review [1] gave the smallest value of 2.5972(7) Å.

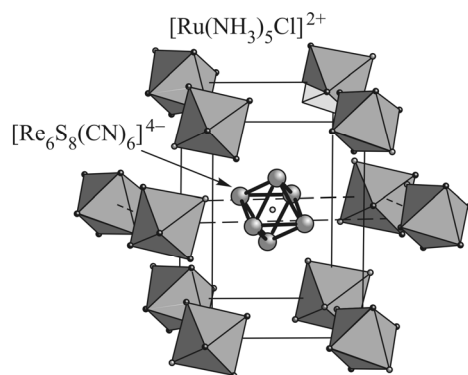
The structure involves two  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$  crystallographically independent complex cations, where the average Ru–N distances (2.100 Å and 2.109 Å) agree well with 2.103 Å in  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  [9], while both values of Ru–Cl (2.338 Å and 2.320 Å) are slightly shorter, 2.346 Å. The deviations of the N–Ru–N bond angles from 90° do not exceed 2.7°, while the deviations of the N–Ru–Cl angles from 180° are also less than 2.7°.

Figure 2 displays the general view of the crystal structure. The pseudohexagonal motif is well seen in the arrangement of the cluster anions, which we discussed previously [6]. The structure is insular, and the shortest N...O distances between the nitrogen atoms that belong to the  $\text{NH}_3$  groups and the oxygen atoms that belong to the crystallization water molecules are 3.02–3.18 Å. The shortest N...O distances between the nitrogen atoms that belong to the CN groups and the oxygen atoms that belong to the crystallization water molecules are 3.20–3.56 Å. Each cluster anion is surrounded by 12 complex cations (Fig. 3), the shortest Ru...Ru distances being of 7.32 Å, Re...Ru 6.47–7.25 Å. Each cation is surrounded by six anions that form a triangular prism, the sides of underlying triangle being of 10.77 Å, 11.72 Å, and 11.59 Å, and its height is 8.71 Å. The N...N distances between the  $\text{NH}_3$  groups of the cations and the CN groups of the anions equal 3.24–3.36 Å.

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**Fig. 2.** Fragment of the crystal structure of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  that demonstrates the pseudohexagonal motif of the mutual arrangement of the  $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$  anions.



**Fig. 3.** Cluster anion surrounded by 12 complex cations.

The atomic coordinates and thermal parameters for the crystal structure of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  have deposited in the German Depositary of Scientific Information in Karlsruhe (Fachinformationszentrum Karlsruhe, B-76344 Eggenstein-Leopoldshafen, Germany; fax: (+49)7247-808-666; e-mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)), ICSD number 417151.

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