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# Double Complex Salts with $[Ru(NH_3)_5Cl]^{2+}$ Cation and $[OsCl_6]^{2-}$ Anion: Synthesis and Properties. Crystal Structure of $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$

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**Abstract**—Double complex salts $[Ru(NH_3)_5Cl][OsCl_6]$ and $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ were prepared and characterized. An X-ray diffraction study showed that $[Ru(NH_3)_5Cl][OsCl_6]$ is isostructural to the previously synthesized $[Rh(NH_3)_5Cl][OsCl_6]$. The structure of $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ was solved by X-ray diffraction ($a = 11.1849(8)$ Å, $b = 7.9528(6)$ Å, $c = 13.4122(9)$ Å; $\beta = 99.765(2)°$; $V = 1175.75$ Å$^3$; space group $C2/m$; $Z = 2$). Thermolysis of the compounds under hydrogen and helium was studied. According to X-ray diffraction, nanosized metallic powders of the corresponding alloys are formed as the final products of thermolysis. The compositions of the obtained solid solutions are consistent with the phase diagram of the Ru–Os system.

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A recent trend for combining subtle investigations of fundamental properties and structures of phases and compounds with the practical use of the results in various multipurpose industrial processes can be noted in chemistry and chemical engineering.

Osmium, which is the heaviest metal (density 22.6 g/cm$^3$), is also among the hardest and high-melting metals. The content of osmium in the Earth crust is only $5 \times 10^{-6}$ wt %; this is a scattered and expensive metal; therefore, it is used in industry only there where minor metal consumption can bring about a considerable effect, for example, to produce premium wear-resistant alloys and as a catalyst. Osmium catalysts are superior to platinum catalysts for hydrogenization of organic compounds [1]. Ruthenium and osmium solid solutions are used as especially strong construction materials [2].

Fusion or high-temperature annealing of finely for preparing homogeneous samples of construction alloys dispersed pure metal powders are used most often for preparing homogeneous samples of construction alloys. This allows one to produce powders over the whole range of compositions. Drawbacks of this method are high annealing temperature (the melting points of pure osmium and ruthenium are 3033 and 2234°C, respectively) and long time (from several days to several weeks) needed to reach the equilibrium. A characteristic feature of osmium is the ability to be oxidized by air oxygen after vacuum sintering of its finely dispersed powder; this complicates the procedure of investigation of the formation of solid solutions by conventional methods [3].

Thermolysis of the coordination compounds containing several metals can be successfully used to obtain solid solutions of refractory metals under rather mild conditions. Previously, we demonstrated the possibility of preparing equilibrium solid solutions of refractory metals by thermolysis of double complex salts (DCS), for example, $Re_{0.5}Os_{0.5}$ [4], $Ru_{0.33}Re_{0.67}$ [5], and $Ru_{0.25}Re_{0.75}$ [6].

The purpose of this work is the synthesis and investigation of the DCS containing Ru and Os, production of solid solutions $Ru_xOs_{1-x}$ by their thermolysis, and analysis of the structural features of metallic phases in the ruthenium–osmium system.

## EXPERIMENTAL

The starting compounds used to produce DCS were $Na_2[OsCl_6]$ and $[Ru(NH_3)_5Cl]Cl_2$ synthesized by published procedures [7, 8].

**$[Ru(NH_3)_5Cl][OsCl_6]$ (I).** Hot (70–80°C) solutions of $[Ru(NH_3)_5Cl]Cl_2$ (0.1 g, $3.42 \times 10^{-4}$ mol) in water (30 mL) and $Na_2[OsCl_6]$ (0.16 g, $3.5 \times 10^{-4}$ mol) in water (40 mL) were mixed. This immediately gave a red-brown precipitate, which was collected, after 3 h, on a fine-porous glass filter under vacuum, washed with water and acetone, and dried in air. IR, cm$^{-1}$: 3289 s, 3230 s, 3179 m ($\nu(NH_3)$); 1613 ($\delta_d(NH_3)$); 1309 s ($\delta_s(NH_3)$); 786 ($\rho_r(NH_3)$); 446 ($\nu$(RuN)). Yield 85-90%.

Anal. calcd. (%): Ru + Os,46.70.

Found (%): Ru + Os, 47.00 ± 0.30.

**$[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ (II).** Finely crystalline $[Ru(NH_3)_5Cl]Cl_2$ (0.13 g, ($4.4 \times 10^{-4}$ mol) was covered by a solution of $Na_2[OsCl_6]$ (0.12 g, $2.57 \times 10^{-4}$ mol) in 0.1 M HCl (40 mL) and allowed to stand in the

**Table 1.** Crystallographic characteristics of the complexes $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ and $[Ru(NH_3)_5Cl][OsCl_6]$

| Formula | $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ | $[Ru(NH_3)_5Cl][OsCl_6]$ |
|---|---|---|
| $a$, Å | 11.1849(8) | 11.593(2) |
| $b$, Å | 7.9528(6) | 8.318(1) |
| $c$, Å | 13.4122(9) | 15.234(3) |
| β, deg | 99.765(2) | 90.707(2) |
| $V$, Å$^3$ | 1175.75 | 1468.97 |
| Space group | $C2/m$ | $P2_1/m$ |
| $Z$ | 2 | 4 |
| FW | 917.18 | 624.62 |
| ρ(calcd.), g/cm$^3$ | 2.564 | 2.824 |

**Table 2.** Atom coordinates in $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ and equivalent thermal parameters

| Atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Os | 0 | 0 | 0.5 | 0.00870(3) |
| Ru | 0.32634(2) | 0 | 0.19796(1) | 0.01015(4) |
| Cl(1) | 0.13459(5) | 0 | 0.09696(4) | 0.0162(1) |
| Cl(2) | 0 | 0.29289(7) | 0.5 | 0.0169(1) |
| Cl(3) | −0.01036(5) | 0 | 0.32307(4) | 0.0155(1) |
| Cl(4) | 0.21094(5) | 0 | 0.52162(4) | 0.0162(1) |
| Cl(5) | 0.17814(5) | 0.5 | 0.12400(4) | 0.0158(1) |
| N(1) | 0.3853(1) | 0.1882(2) | 0.1056(1) | 0.0163(3) |
| N(2) | 0.2653(1) | 0.1850(2) | 0.2903(1) | 0.0151(3) |
| N(3) | 0.5001(2) | 0 | 0.2877(2) | 0.0183(4) |

**Table 3.** Selected interatomic distances ($d$) and bond angles (ω) for $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$*

| Bond | $d$, Å | Angle | ω, deg |
|---|---|---|---|
| Os–Cl(2) | 2.3293(6) | Cl(3)OsCl(4) | 89.94(2) |
| Os–Cl(3) | 2.3561(6) | N(3)RuN(1) | 89.18(6) |
| Os–Cl(4) | 2.3278(6) | N(1)RuN(1)# | 89.90(8) |
| Ru–N(1) | 2.1181(15) | N(1)RuN(2)# | 179.10(6) |
| Ru–N(2) | 2.1094(14) | N(3)RuN(2) | 91.37(6) |
| Ru–N(3) | 2.105(2) | N(1)RuN(2) | 90.82(6) |
| Ru–Cl(4) | 2.3344(6) | N(2)#RuN(2) | 88.46(8) |
| | | N(3)RuCl(1) | 179.41(6) |
| | | N(1)RuCl(1) | 90.40(4) |
| | | N(2)RuCl(1) | 89.06(4) |

* Symmetry operations used for generation of equivalent atoms: # $x$, $-y - 1$, $z$.

dark for 5 days. After this period, the starting $[Ru(NH_3)_5Cl]Cl_2$ completely dissolved, and dark claret-colored crystals precipitated from the solution. The precipitate was collected on a porous glass filter, washed with water and acetone, and dried in air. IR, cm$^{-1}$: 3282 s, 3163 s, 3087 m, (ν($NH_3$)); 1615 ($\delta_d$($NH_3$)); 1305 s ($\delta_s$($NH_3$)); 786 ($\rho_r$($NH_3$)); 448 (ν(RuN)). Yield 85–90%.

Anal. calcd. (%): Ru + Os, 42.80.

Found (%): Ru + Os, 42.60 ± 0.30.

IR spectra were recorded on a Scimitar FTS 2000 FT IR spectrometer in the 400–4000 cm$^{-1}$ range (KBr pellets). The sum of the metals was quantified by heating an exact weighed portion of DCS under hydrogen or helium to 500°C.

The thermal properties were studied on a Q-1000 derivatograph. A ~100-mg sample of the compound was placed into a quartz crucible without a lid and heated at a rate of 10 K/min in a helium flow (150 mL/min).

X-Ray diffraction analysis of polycrystalline DCS was carried out on a DRON-3M diffractometer (Cu$K_\alpha$ radiation, Ni filter, $2\theta = 5°–60°$). All the synthesized samples were single phases.

X-Ray diffraction analysis of the metallic thermolysis products was carried out on a DRON-SEIFERT-RM4 diffractometer (Cu$K_\alpha$ radiation, Ni filter, $2\theta = 5°–160°$) at room temperature under atmospheric pressure. The products were triturated in heptane and the suspension was applied onto the polished side of a standard quartz cell. The samples thus obtained were ~100 μm thick layers. A polycrystalline silicon sample prepared in a similar way was used as the reference. The X-ray diffraction patterns were indexed by analogy with X-ray diffraction patterns of pure metals [9]. Using the PowderCell 2.4 program [10] (the peak profiles were fitted by an asymmetric Lorentz function, $2\theta = 30°–150°$), the unit cell parameters (UCP) were refined.

Single crystal X-ray diffraction analysis of **II** (UCP refinement and diffraction reflection intensity measurement) were carried out on a BRUKER X8APEX diffractometer (Mo$K_\alpha$ radiation, graphite monochromator, CCD detector, room temperature, $\theta = 3.08°–32.55°$, 2251 experimental reflections). The crystal structure was refined in the full-matrix approximation for 2228 independent reflections to $R = 0.0154$ for all reflections and $R = 0.0152$ for the reflections with $I > 2\sigma(I)$. The hydrogen atoms were specified geometrically in idealized positions. The UCP are summarized in Table 1, atom coordinates and thermal vibrations are given in Table 2, and the interatomic distances and bond angles are given in Table 3.

## RESULTS AND DISCUSSION

**Synthesis.** Due to the low solubility and high thermodynamic stability of the complex ions, all of the

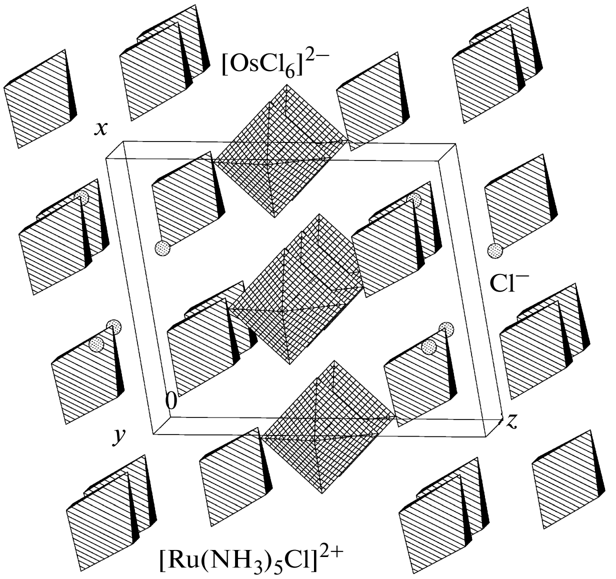

**Fig. 1.** General view of the $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ structure along the *y* axis.

obtained DCS are formed from aqueous solutions in high yields. It was found by powder X-ray diffraction that product **I** was a single phase. The phase composition of product **II** depends on the conditions of synthesis. After keeping the starting components in hydrochloric acid for 3 days, the target product contained (according to powder X-ray diffraction data) about 20% of **I** as an impurity, and after the system was kept for 5 days, the residual **I** was completely converted to complex **II**. The nature of equilibria in the formation of phases of this type from aqueous solutions was considered previously [11].

**Crystal structure of salts I and II.** According to powder and single crystal X-ray diffraction, compound **II** is isostructural to the series of DCS $[M^I(NH_3)_5Cl]_2[M^{II}Cl_6]Cl_2$, where $M^I$ = Rh, Ir, Co; $M^{II}$ = Re, Os, Ir, Pt [12]. The interatomic distances within the coordination polyhedra do not differ from these distances in other salts containing the same complex ions. The Os–Cl bond lengths in the complex anion are 2.328–2.356 Å, those in the complex cation are: $(Ru–N)_{avg}$, 2.111; Ru–Cl, 2.334 Å. The metal–metal distances also do not differ from the distances characteristic for this series of isostructural compounds. The shortest Ru···Os distance is 5.773 Å. The general view of the structure along the *y* axis is shown in Fig. 1.

The UCP of complex **I** were refined by powder X-ray diffraction data using full-profile analysis. The structure $[Rh(NH_3)_5Cl][OsCl_6]$ described previously [13] was used as the model. According to X-ray diffraction data, $a$ = 11.5931(4) Å, $b$ = 8.3181(3) Å, $c$ = 15.2344(4) Å; $\beta$ = 90.707(4)°; $V$ = 1469 Å$^3$; space group $P2_1/m$; $Z$=4.

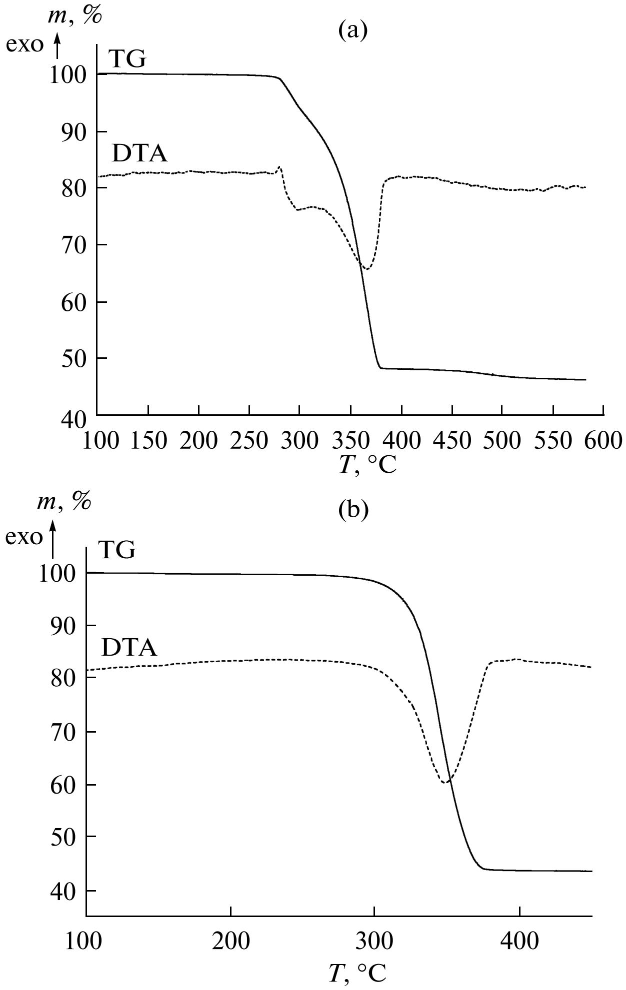

**Fig. 2.** Weight-loss TG and DTA curves recorded under helium (10 K/min) for (a) $[Ru(NH_3)_5Cl][OsCl_6]$, (b) $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$.

**Thermal decomposition.** Decomposition of complex **I** under helium includes several poorly separated stages, as indicated by the DTA curve. The decomposition is mainly completed at 380°C, the weight loss being 1.7% greater than the theoretical value. The remaining mass gradually decreases on further heating to 540°C. This process remains uninterpreted as yet. The pattern of decomposition of **II** under helium is simpler: one-stage decomposition starts at 300°C and ends at 380°C. The weight loss nearly corresponds to the formation of the sum of metals (Fig. 2). As noted previously, decomposition processes in a hydrogen atmosphere occur faster; this is also true for these compounds. Thus, the temperatures for preparating metallic solid solutions are about 1/5 of the melting points of pure metals.

**Thermolysis products.** Single-phase solid solutions are formed as the final products of decomposition of DCS under both helium and hydrogen. For **I**, this is $Ru_{0.5}Os_{0.5}$ and for **II**, this is $Ru_{0.67}Os_{0.33}$.

**Table 4.** Crystallographic data for metallic phases in the Ru–Os systems and conditions for their preparation

| Composition | Preparation conditions | $a$, $c$, Å | $V/Z$, Å$^3$ |
|---|---|---|---|
| Ru<br>[9, no. 6-663] | Reference | 2.7058*<br>4.2819 | 13.575 |
| $Ru_{0.88}Os_{0.12}$<br>[16] | Alloying at 2000°C, vacuum | 2.705<br>4.274 | 13.54 |
| $Ru_{0.74}Os_{0.26}$<br>[16] | Alloying at 2000°C, vacuum | 2.710<br>4.288 | 13.64 |
| $Ru_{0.67}Os_{0.33}$<br>[This work] | $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$, 650°C, $H_2$, annealing for 5 h | 2.714(2)<br>4.297(3) | 13.71 |
| $Ru_{0.67}Os_{0.33}$<br>[This work] | $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$, 650°C, He, 1 h | 2.716(2)<br>4.298(3) | 13.73 |
| $Ru_{0.56}Os_{0.44}$<br>[16] | Alloying at 2000°C, vacuum | 2.716<br>4.297 | 13.73 |
| $Ru_{0.5}Os_{0.5}$<br>[This work] | $[Ru(NH_3)_5Cl][OsCl_6]$, 650°C, $H_2$, annealing for 5 h | 2.716(2)<br>4.302(3 | 13.74 |
| $Ru_{0.5}Os_{0.5}$<br>[This work] | $[Ru(NH_3)_5Cl][OsCl_6]$, 650°C, He, 1 h | 2.718(2)<br>4.304(3) | 13.768 |
| $Ru_{0.5}Os_{0.5}$<br>[15] | Alloying** | 2.719*<br>4.302 | 13.77 |
| $Ru_{0.32}Os_{0.68}$<br>[16] | Alloying at 2000°C, vacuum | 2.721<br>4.308 | 13.81 |
| Os<br>[9, no. 6-662] | Reference | 2.7341*<br>4.3197 | 13.98 |

Notes: * The error of determination of the parameters is not indicated in the cited study.
** The exact temperature and alloying conditions are not reported.

The phase diagram of the Ru–Os system [14] is characterized by a continuous series of hexagonal solid solutions. The volume per atom for the solid solutions decreases in an additive fashion on increase in the Ru content with simultaneous decrease in the melting point. The UCP values and the melting points of the pure components reported in [14] are somewhat greater than the data of [15] and [16]. This may be due to different purities of the initial metals and differenct accuracies of determination of the UCP. Generally, the solid solutions of Os and Ru have not been adequately studied. We were able to find only several mentions of the crystallographic data concerning this system in the literature. These data for Ru–Os alloys known in the literature are summarized in Table 4.

For analysis of a binary metallic system, it is convenient to use the curve for the volume per atom ($V/Z$) as a function of the solid solution composition (Retgers curve). For the Ru–Os system, this curve was constructed from published data [9, 15, 16] and our results (Fig. 3). For better understanding, it is recommended to consider Fig. 3 simultaneously with Table 4. The points that we obtained (pointed to by arrows with indication of the precursor DCS and thermolysis conditions) are well correlated with characteristics of analogous samples obtained by alloying. Together with our data on total metal contents, this confirms the composition of the obtained phases: $Ru_{0.5}Os_{0.5}$ and $Ru_{0.67}Os_{0.33}$.

The points calculated from published data and obtained in this work are adequately fitted by second-order polynomial: $y = 13.57 + 0.30x + 0.10x^2$. The negative deviation from the linearity is not more than 0.6%; that is the Rutgers rule of the linear dependence of the volume per atom in a solid solution on the composition is closely obeyed. Note that the UCP of the thermolysis products that we studied correlate with the UCP of real alloys. For example, the UCP for the phase $Ru_{0.5}Os_{0.5}$ that we obtained at 650°C in a He atmosphere ($a = 2.718(2)$, $c = 4.304(3)$ Å) and the UCP of the $Ru_{0.5}Os_{0.5}$ phase obtained previously [15] by alloying at 2000°C ($a = 2.719$ Å, $c = 4.302$ Å).

Thus, DCS $[Ru(NH_3)_5Cl][OsCl_6]$ and $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ have been synthesized. It has been shown that their thermolysis under helium and hydrogen at 600–650°C is accompanied by the formation of nanocrystalline single-phase metallic powders $Ru_{0.5}Os_{0.5}$ and $Ru_{0.67}Os_{0.33}$. Their $V/Z$ characteristics are well correlated with the characteristics of alloys of similar composition reported in the literature. It has been found that $[Ru(NH_3)_5Cl]_2[OsCl_6]Cl_2$ is isostructural to a large series of DCS with the general formula

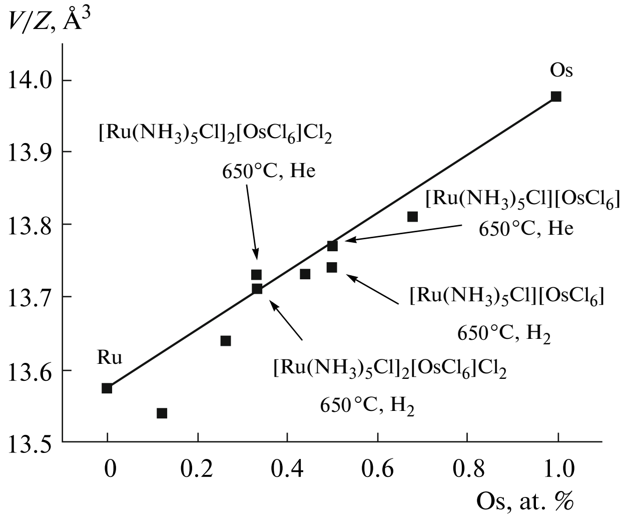

**Fig. 3.** $V/Z$ vs. composition for solid solutions $Ru_xOs_{1-x}$ (for the legend, see Table 4). The arrows are directed to the points obtained in this study (the synthesis conditions and starting DCS are indicated nearby).

$[M^I(NH_3)_5Cl]_2[M^{II}Cl_6]Cl_2$, where $M^I$ = Rh, Ir, Co; $M^{II}$ = Re, Os, Ir, Pt.

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