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SYNTHESIS AND CRYSTAL STRUCTURE OF [Cr(NH$_3$)$_5$Cl][PdBr$_4$]

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A new binary complex salt — chloropentaamminechromium(III) tetrabromopalladate(II) [Cr(NH$_3$)$_5$Cl][PdBr$_4$] — has been synthesized. The compound was characterized by elemental, X-ray diffraction, and X-ray phase analysis. The salt is isostructural with the previously investigated compounds [M(NH$_3$)$_5$Cl][PtCl$_4$] (M = Ir, Rh, Ru, Co, Cr) and [CM(NH$_3$)$_5$Cl][PdBr$_4$] (M = Ir, Rh, Co). Crystallographic data: space group *Pnma*, $a = 17.068(2)$ Å, $b = 8.315(12)$ Å, $c = 9.653(14)$ Å; $V = 1370.0(3)$ Å^3, $Z = 4$, $d_{\text{calc}} = 2.903$ g/cm^3.

Keywords: chromium, palladium, chloropentaammine, bromine complexes, X-ray phase analysis, X-ray diffraction analysis, crystal chemistry.

Salts with complex cations and anions and different elements as the central atom, called binary complex salts (below referred to as BCS), are efficient precursors for the synthesis of nanosized metal powders [1]. We have previously investigated BCS polycrystals containing chloropentaammines of Co(III), Rh(III), and Ir(III) as cations and tetrabromopalladate(II) as the anion [2]. It was established that these compounds are isostructural with each other and with [Ir(NH$_3$)$_5$Cl][PtCl$_4$] investigated in [3]. The goal of the present work was to establish the crystal structure of the BCS containing the tetrabromopalladate(II) anion [Cr(NH$_3$)$_5$Cl][PdBr$_4$].

Experimental. The starting [Cr(NH$_3$)$_5$Cl]Cl$_2$ and K$_2$[PdBr$_4$] complexes were synthesized using the standard procedures [2, 4]. The resulting [Cr(NH$_3$)$_5$Cl]Cl$_2$ was transformed into the corresponding bromide by dissolving it in a minimal amount of water and subsequently precipitating the product with an excess of KBr. To obtain the BCS under investigation, an equimolar amount of [Cr(NH$_3$)$_5$Cl]Br$_2$ dissolved in the minimal amount of water (~0.01 M) was added to the 0.01 M solution of K$_2$[PdBr$_4$] in 0.1 M KBr. The solutions were mixed, and a wine-colored fine crystalline precipitate formed immediately. After cooling the reaction mixture to 0°C, the precipitate was filtered off and washed with ~1 ml of water and then with acetone. The yield of the product was 70%. Analysis for metals was carried out by atomic absorption spectrophotometry with flame atomization (Hitachi Z-8000 instrument). Found, %: Cr 8.8, Pd 17.8. Calculated for H$_{15}$N$_5$Br$_4$ClCrPd, %: Cr 8.7, Pd 17.8.

The precipitate contained several single crystals suitable for an X-ray structural analysis. They were separated using the following procedure. A small amount of ethanol was poured on the precipitate, the mixture was stirred, and the resulting suspension was immediately decanted. The largest crystals settled at the bottom. The procedure was repeated several times; then the crystals were dried on filter paper.

X-ray phase analysis showed that the product was a single phase. Recording was carried out with a DRON-RM4 diffractometer (CuK_α radiation, Ni filter, scintillation detector with amplitude discrimination). The sample was prepared by depositing a heptane suspension onto the polished side of a standard quartz cell, followed by drying. The external reference was a polycrystalline silicon sample ($a = 5.4309$ Å) prepared using the same procedure. The diffraction patterns were

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recorded in a stepwise mode in the 2θ range from 5° to 55°. It was established that the $[Cr(NH_3)_5Cl][PdBr_4]$ complex is isostructural with the $[M(NH_3)_5Cl][PtCl_4]$ (M = Ir, Rh, Ru, Co, Cr) [1] and $[M(NH_3)_5Cl][PdBr_4]$ (M = Ir, Rh, Co) [2] complexes.

The single crystal was investigated with a Bruker X8 APEX *P*4 automatic diffractometer (MoK_α radiation, graphite monochromator). Crystallographic data for $[Cr(NH_3)_5Cl][PdBr_4]$ and characteristics of X-ray experiment are listed in Table 1. Atomic coordinates are shown in Table 2; interatomic distances and bond angles are listed in Table 3. All calculations were carried out with the SHELX-97 software package [5].

Description of the crystal structure. The crystal structure of the $[Cr(NH_3)_5Cl][PdBr_4]$ binary complex salt is composed of discrete $[Cr(NH_3)_5Cl]^{2+}$ cations, which are distorted octahedra, and discrete plane square anions $[PdBr_4]^{2-}$. The structural units with atomic numbering and thermal vibration ellipsoids are shown in Fig. 1 (hydrogen atoms are omitted). A view of the crystal structure in the direction of the *Y* axis is shown in Fig. 2. Each cation is surrounded by six anions, and vice versa. Thus the structure can be related to a distorted NaCl type.

TABLE 1. Crystal Data for $[Cr(NH_3)_5Cl][PdBr_4]$ and Characteristics of X-Ray Diffraction Experiment

Formula	$[Cr(NH_3)_5Cl][PdBr_4]$
Molecular mass	598.66
Space group	*Pnma*
a, b, c, Å	17.068(2), 8.3150(12), 9.6528(14)
V, Å^3	1370.0(3)
d_{calc}, g/cm^3	2.903
Z	4
θ range	2.39-23.30°
No. of reflections total/independent	5665/1071
R_1 and wR_2 for $I > 2\sigma_I$	0.0449, 0.1040
R_1 and wR_2 for all I	0.0494, 0.1061

TABLE 2. Atomic Coordinates (×10^4) and Equivalent Thermal Parameters (Å^2×10^3)

Atom	x/a	y/b	z/c	U_{eq}	Atom	x/a	y/b	z/c	U_{eq}
Pd	1570(1)	2500	8446(1)	24(1)	Cr	971(1)	2500	3629(2)	21(1)
Br1	246(1)	2500	9323(1)	34(1)	Cl	–79(2)	2500	5170(3)	35(1)
Br2	1549(1)	–401(1)	8500(1)	55(1)	N1	1846(9)	2500	2180(13)	42(3)
Br3	2896(1)	2500	7466(1)	40(1)	N2	1539(4)	717(9)	4787(7)	37(2)
					N3	446(5)	719(8)	2491(7)	37(2)

TABLE 3. Interatomic Distances d (Å) and Bond Angles ω (deg)

Distance	d	Angles	ω	Distance	d	Angles	ω
Pd–Br2	2.4128(11)	Br2–Pd–Br1	88.80(3)	Cr–N3	2.050(7)	N1–Cr–N3	87.3(4)
Pd–Br1	2.4129(16)	Br2–Pd–Br3	91.23(3)	**⟨Cr–N⟩**	**2.063**	N3–Cr–Cl	90.3(2)
Pd–Br3	2.4538(16)	Br1–Pd–Br3	177.86(6)			N2–Cr–Cl	90.9(2)
⟨Pd–Br⟩	**2.427**	Br2a–Pd–Br2	177.03(7)	Cr–Cl	2.329(3)	N3–Cr–N3a	92.5(4)
						N2a–Cr–N2	90.1(4)
Cr–N1	2.046(12)	N1–Cr–N2	91.6(4)			N3a–Cr–N2	178.3(3)
Cr–N2	2.095(7)	N3–Cr–N2	88.7(3)			N1–Cr–Cl	176.6(4)

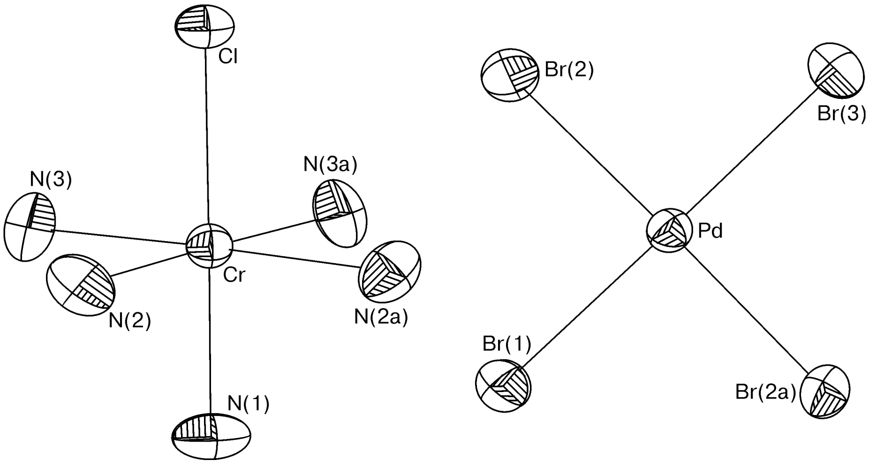

Fig. 1. Structural units with atomic numbering.

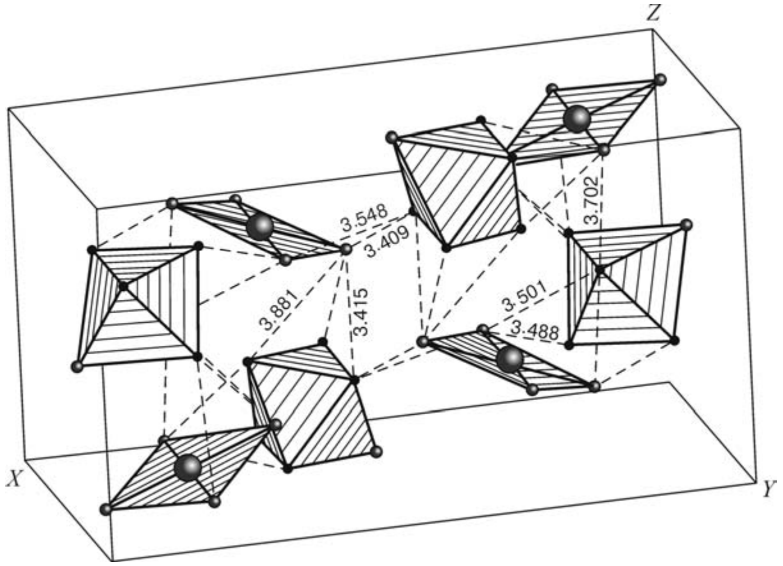

Fig. 2. General view of the crystal structure of $[Cr(NH_3)_5Cl][PdBr_4]$. Dashed lines mark the shortest Br…NH_3 contacts with indications of Br…N distances.

If we compare the geometry of the $[Cr(NH_3)_5Cl]^{2+}$ complex cations in the given structure and in $[Cr(NH_3)_5Cl]Cl_2$ [6], we can notice that the N–Cr–Cl angle has changed significantly: 176.6° and 179.4°, respectively. The Cr–Cl bond length remains almost unchanged: 2.327 Å and 2.329 Å, respectively.

The arrangement of complex anions in crystal is chainlike (Fig. 3). The distances between the nearest bromine atoms in a chain are 3.49 Å, while the sum of the van der Waals radii of the bromide ions is 3.94 Å [7]. This is evidence of specific intermolecular interactions. The coordination polyhedron is distorted in comparison with $K_2[PdBr_4]$ [8]: the Br–Pd–Br bond angles deviate by 1.2° from 90°, while the mean length of the Pd–Br bond decreases from 2.444 Å to 2.437 Å.

The shortest N…Br distances between ions are 3.409 Å and 3.415 Å, which suggests hydrogen bonding between the bromine and hydrogen atoms belonging to the ammonia ligand. Thus it may be assumed that the structure is stabilized by additional interactions between the complex cations and anions.

The Pd…Cr distances are 4.761 Å, 5.107 Å, 5.911 Å, and 6.332 Å, while the shortest Pd…Pd and Cr…Cr distances are 7.118 Å and 5.939 Å, respectively. The mutual arrangement of the metal atoms in the structure is shown in Fig. 4. In

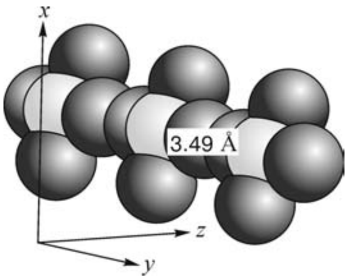

Fig. 3. Formation of chains from anions in the direction of the *Y* axis. White balls: Pd atoms, gray balls: Br atoms. The Br…Br distance is shown.

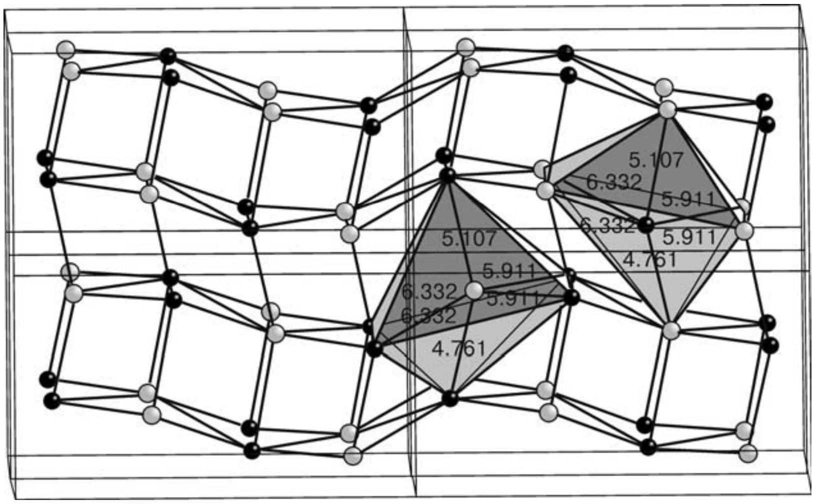

Fig. 4. Mutual arrangement of the central atoms in the structure of $[Cr(NH_3)_5Cl][PdBr_4]$. White balls: Pd atoms, black balls: Cr atoms. The pseudooctahedral surroundings of each atom with indications of Cr…Pd distances are shown.

$[Cr(NH_3)_5Cl]Cl_2$, the Cr…Cr distances are 6.428 Å; in $K_2[PdBr_4]$, the Pd…Pd distances are 4.446 Å. Thus the palladium atoms, having no additional coordination in the structure, are widely separated from one another. A similar situation is observed in the structure of $[Cr(NH_3)_5Cl][PdCl_4]\cdot H_2O$ [9]: Pd…Pd 5.49 Å and Cr…Cr 6.23 Å.

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