Crystal Chemistry of Octahedral Rhodium(III) Chloroamines

K. Yusenko

Institute for Geology, Mineralogy and Geophysics, Ruhr-University Bochum, Germany
kirill.yusenko@rub.de

Rhodium(III) octahedral complexes with amine and chloride ligands are the most common starting compounds for preparing functional and catalytically active rhodium(I) and rhodium(III) species. Despite intensive study during the last 100 years, synthesis and crystal structures of rhodium(III) complexes were described only sporadically. Some $[RhCl_x(NH_3)_{6-x}]$ compounds are still unknown. In the current report, available information about crystal structures of possible $[RhCl_x(NH_3)_{6–x}]$ octahedral species are summarized and critically analysed. Unknown crystal structures of $(NH_4)_2[Rh(NH_3)Cl_5]$, *trans*–$[Rh(NH_3)_4Cl_2]Cl×H_2O$, and *cis*–$[Rh(NH_3)_4Cl_2]Cl$ are reported based on high quality single crystal X-ray diffraction data. Octahedral complexes $[RhCl_x(NH_3)_{6-x}]$ are important models to study crystal packings of hard cations and anions and their dependence on coordination environment. Here, symmetry, packing, short contacts and hydrogen bonds in a broad class of coordination compounds are analysed in details.

The crystal structures of $(NH_4)_2[Rh(NH_3)Cl_5]$, *trans*–$[Rh(NH_3)_4Cl_2]Cl×H_2O$, $[Rh(NH_3)_5Cl]Cl_2$, and $[Rh(NH_3)_6]Cl_3$ have face-centered cubic arrangement of closed-packed hexagonal layers (Figure 1). Such an arrangement could be easily described based on pseudo- translational sublattices developed for structures with large cations. In all mentioned salts, pseudo-translational sublattices had similar metrics. Directions of pseudo-translational vectors gave the orientation of the closed-packed layers in their crystal structures. It is important to note that the crystal structures of $(NH_4)_2[Rh(NH_3)Cl_5]$ and $[Rh(NH_3)_5Cl]Cl_2$ were similar. It is possible that this is a general tendency in coordination chemistry, which should be proven for other classes of isoformular coordination compounds. Such a phenomenon might be useful as a tool for crystal structure prediction and preparation of double complexes.

The Rh(III) chloroamine complexes did not realize the maximal possible symmetry of coordination polyhedrons. Deformations of the coordination polyhedrons depended not only on the ligand arrangements, but also possibly on the packings of deformed octahedrons in the crystal structures. Closed-packings are typical for such structurally rigid coordination species, but local structure and symmetry of coordination polyhedrons usually fit the packings of hexagonal packed layers. Changes in the interatomic distances were also high due to trans-effect in cis- and trans-isomers. If specific interactions could be realized in the crystal structures (similar to *fac*–$[Rh(NH_3)_3Cl_3]$) due to sterically-driven factors, then close-packed arrangements could possibly distort with a formation of other types of packings.

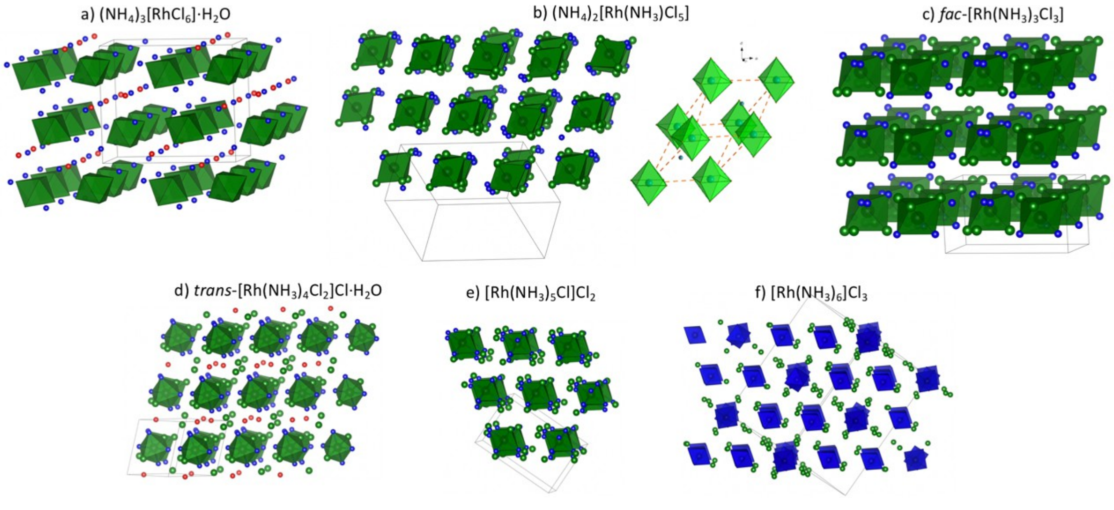

Figure 1. Crystal structures of $[RhCl_x(NH_3)_{6-x}]$ species: (**a**) $(NH_4)_3[RhCl_6]×H_2O$ along *b*-direction, two layered hexagonal closed-packed layers are formed perpendicular to the *a*-direction; (**b**) three layered face-centered closed packing in $(NH_4)_2[Rh(NH_3)Cl_5]$, corresponding pseudo-translational sub-lattice is shown; (**c**) crystal structure of *fac*–$[Rh(NH_3)_3Cl_3]$ along the *c*-direction, hexagonal layers can be found perpendicular to the *a*-direction; three layered face-centered closed packing in crystal structure of *trans*–$[Rh(NH_3)_4Cl_2]Cl×H_2O$ (**d**), $[Rh(NH_3)_5Cl]Cl_2$ (**e**), and $[Rh(NH_3)_6]Cl_3$ (**f**) (Rh atoms are shown as black circles, N atoms are blue, Cl atoms are green, and H atoms are omitted for clarity).