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Seven-Coordinate Ruthenium Atoms Sequestered in Praseodymium Clusters in the Chloride $\{RuPr_3\}Cl_3$

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The first example for an endohedral transition-metal atom (Ru) sequestered in a seven-coordinate surrounding of rare-earth metal atoms (Pr) has been found for $\{RuPr_3\}Cl_3$. The monocapped trigonal prisms of Pr atoms share two rectangular faces, forming a zigzag chain with Ru−Ru distances of 308 pm. Intracluster bonding is dominated by Ru−Pr bonding with very little Ru−Ru bonding.

There is a steadily increasing number of new, even novel, reduced rare-earth metal (M) halides (X) with clusters incorporating endohedral atoms Z.[1] These interstitials are main-group, e.g., C, N, O, or transition-metal atoms, e.g., Fe, Ru, Os. The coordination number of the endohedral atom is mostly six (octahedral or, less frequently, trigonal prismatic or in between). $\{CSc_6\}I_{12}Sc$[2] and $\{Ru_4Y_{16}\}X_{20}$ (X = Br, I)[3] are examples. O, N, and sometimes C atoms adopt coordination number 4 (tetrahedral); $\{OLa_4\}Br_7$[4] and $\{Sc_4C_{10}Sc_{20}\}_{30}$[5] may serve as examples. Coordination numbers higher than 6 are still rare. The first example was seen in $\{OsY_{8/2}\}Br_4$[6] with eight-coordinate Os atoms in square antiprisms of Y atoms sharing common faces; all Os−Os distances are equal. Another recent example is $\{Ir_3Sc_{12}\}Br_{16}$,[7] where $IrSc_8$ square antiprisms and cubes in a 2:1 ratio share common faces, forming a chain in which the Ir−Ir distances are not equal, and an Ir−Ir bond (d = 283 pm) must be stated for such Ir atoms, which occupy two neighboring square antiprisms.

We have now, for the first time, observed with $\{RuPr_3\}Cl_3$ a reduced rare-earth metal halide with a seven-coordinate endohedral atom. Black single crystals were obtained from the reaction of $PrCl_3$, Pr, and Ru.[8,9] The crystal structure was determined from single-crystal X-ray diffraction data.[10]

In $\{RuPr_3\}Cl_3$, the Ru atom as the central atom of an *anti-Werner* complex,[11] is surrounded by seven Pr atoms at distances of 274.5(1) (Ru−Pr2, 2×), 277.2(1) (Ru−Pr1, 2×; upper rectangular face, see Figure 1), 325.9(2) (Ru−Pr1), 337.7(2) (Ru−Pr3, cap), and 351.5(2) (Ru−Pr2) pm. This constitutes a rather heavily distorted monocapped trigonal

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(8) Synthesis: A mixture of 200 mg of $PrCl_3$ (synthesized by the ammonium chloride route and purified as described previously),[9] 85.5 mg of Pr (Chempur, Karlsruhe, Germany, 99.9%), and 40.8 mg of Ru (Merck, Darmstadt, Germany, 99.9%) was filled in a tantalum ampule, which was He-arc-sealed and jacketed with a silica ampule. The temperature program used was as follows: 1000 °C for 5 days and cooling at 2 °C/h to 700 °C and then at 10 °C/h to room temperature. All manipulations were carried out under strict exclusion of air and especially moisture in a drybox (MBraun, Garching, Germany). Black crystals were selected under a microscope in a drybox and sealed in thin-walled glass capillaries.

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(10) Crystal data for $\{RuPr_3\}Cl_3$: diffractometer IPDS-I, Stoe, Darmstadt, Germany; Mo Kα (graphite monochromator, $\lambda = 71.073$ pm); $T = 293(2)$ K; $\theta_{max} = 28.2°$; $0° \le \varphi \le 200°$, $\Delta\varphi = 2°$, 100 images; $-18 \le h \le 18$, $-4 \le k \le 4$, $-16 \le l \le 16$; $\rho_{calcd} = 5.477$ g cm^{-3}; 814 measured reflections, of which 581 were symmetrically independent; $R_{int} = 0.096$; $F(000) = 1020$; $\mu = 22.569$ mm^{-1}, orthorhombic, *Pnma* (No. 62), $a = 1432.3(3)$ pm, $b = 400.42(6)$ pm, $c = 1257.6(2)$ pm, $V = 721.3(2) \times 10^6$ pm^3, $Z = 4$; R1/wR2 for 581 reflections with $[I_0 > 2\sigma(I_0)]$ 0.0392/0.0974, for all data 0.0589/0.1030; GOF = 1.368.

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10.1021/ic800907c CCC: $40.75

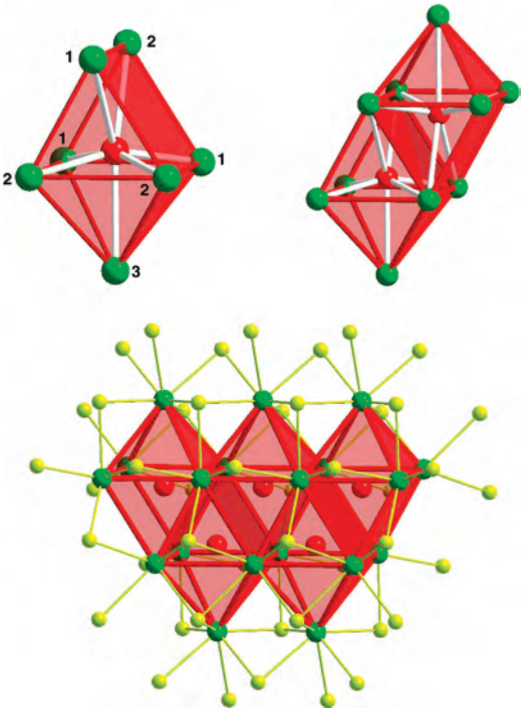

Figure 1. $RuPr_7$ cluster with Pr atoms numbered (above, left), two $RuPr_7$ clusters sharing one rectangular face (above, right), and part of the infinite zigzag chain of face-sharing monocapped trigonal antiprisms $RuPr_{6/3}Pr$ surrounded by Cl atoms (below) in the crystal structure of $\{RuPr_3\}Cl_3$.

prism with an average Ru−Pr distance of 302.6 pm. In contrast, in $\{RuPr_3\}I_3$ with six-coordinate ruthenium ($RuPr_6$ octahedra share common edges to a double chain), the Ru−Pr distances lie in a very narrow range and average to 284.8 pm.[12] The isostructural $\{RuPr_3\}Br_3$ was identified by powder X-ray diffraction only.[13]

The monocapped trigonal prisms share two common rectangular faces in $\{RuPr_3\}Cl_3$, in accordance with the *Niggli* formulation $\{RuPr_{6/3}Pr_{1/1}\}Cl_3$; see Figure 1. The shared rectangular faces have edge lengths of 364.7(2) and 392.6(1) pm. Pr−Pr distances in the nonshared edges range from 382 to 405 pm.

The $RuPr_{6/3}Pr$ chains run down the crystallographic *b* axis, whose length [400.42(6) pm] is identical with the Pr1−Pr2 edge length of the rectangular face that is capped by Pr3. The chains are arranged in the fashion of a hexagonal closest packing of rods, although compressed in the [100] direction; see Figure 2.

The $RuPr_{6/3}Pr$ chains are surrounded by Cl atoms, which also connect them, as Figure 2 shows. Pr−Cl distances range between 288 and 326 pm. These distances correlate very well with the mean distance in $PrCl_3$ itself, 291.5 pm.[14] Thus, Pr−Cl bonding must be predominantly ionic.

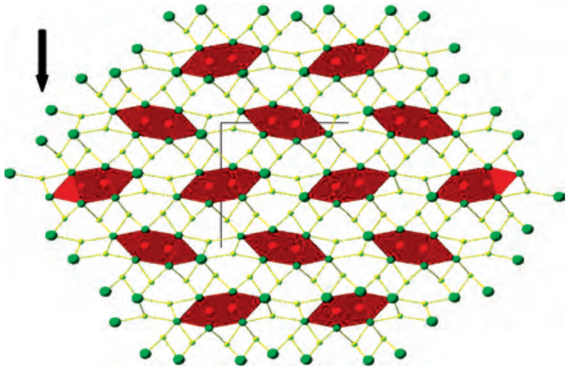

Figure 2. Arrangement of the $RuPr_{6/3}Pr$ chains separated by and connected through Cl atoms in $\{RuPr_3\}Cl_3$. Projection onto (010); the arrow indicates the [100] direction.

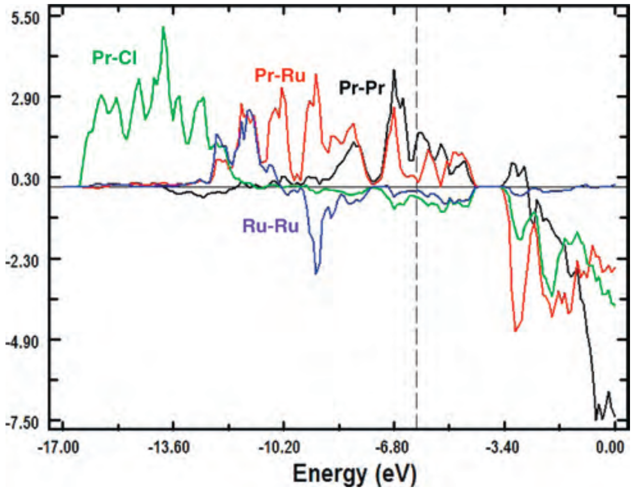

Figure 3. COOPs for $\{RuPr_3\}Cl_3$. Positive values represent bonding interactions and negative values antibonding interactions. Green curves represent Pr−Cl (14×), blue Ru−Ru (2×), red Pr−Ru (7×), and black Pr−Pr (10×) interactions.

Calculations of the electronic structure of $(RuPr_3)Cl_3$ were performed by making use of the extended Hückel method.[15] The crystal orbital overlap population (COOP) analysis of the results of these calculations is shown in Figure 3. Pr−Cl bonding interactions are indeed low in energy ("ionic"), although there are some minor antibonding contributions when approaching the Fermi level. Ru−Ru bonding certainly plays a role, but there is considerable Ru−Ru antibonding closer to the Fermi level, which not quite but almost outweighs the bonding interactions lower in energy. Pr−Ru interactions are always bonding and certainly stronger (lower in energy and in total) than Pr−Pr bonding. Pr−Ru and Pr−Pr interactions are still bonding above the Fermi level, which lies at a local minimum of the density of states. A pseudo band gap, above which there are (almost) completely antibonding interactions, occurs well above the Fermi level. In summary, bonding in $(RuPr_3)Cl_3$ is dominated by ionic Pr−Cl as well as by (covalent) Pr−Ru interactions. This

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(15) Semi-empirical extended Hückel calculations (EH) were performed with the program package CAESAR [Ren, J.; Liang, W.; Whangbo, M.-H. *CAESAR*; PrimeColor Software Inc.: Raleigh, NC, 1998]. using double-ζ functions with the following parameters: H_{ij} [eV], ζ_1, coefficient 1, ζ_2, coefficient 2. For Pr: 6s, −5.69, 1.7, 0.5671, 1.0, 0.5503; 6p, −2.88, 1.34, 1.0, 0.0, 0.0; 5d, −6.4, 2.55, 0.52, 1.2, 0.64; 4f, −6.12, 8.9, 0.4172, 4.35, 0.729. For Ru: 5s, −8.43, 1.95, 0.5538, 1.05, 0.5668; 5p, −3.49, 1.42, 1.0, 0.0, 0.0; 4d, −10.1, 3.45, 0.5394, 1.5, 0.6062. For Cl: 3s, −26.67, 2.9, 0.6262, 1.75, 0.5051; 3p, −13.85, 2.45, 0.5554, 1.3, 0.5519. COOP analysis (Wijeyesekera, S.; Hoffmann, R. *Organometallics* **1984**, *3*, 949) was used to interpret the chemical bonding.

pattern very well follows the electron affinities of Ru (−101 kJ/mol), Pr (≤−50 kJmol), and Cl (−349 kJ/mol).[16]

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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