Inorganic Chemistry
Communication

Inorg. Chem. **2010**, 49, 5347–5349 **5347**
DOI: 10.1021/ic100487k

Chains of Face-Sharing $\{ZPr_6\}$ Octahedra with Alternating Endohedral Iridium Atoms and Chloride Ions in $\{(Ir,Cl)Pr_6\}Cl_{10}$

Nina Herzmann,[†] Matthias Brühmann,[†] Anja-Verena Mudring,[‡] and Gerd Meyer*[,†]

[†]*Department of Chemistry, Inorganic Solid State and Coordination Chemistry, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany, and* [‡]*Faculty of Chemistry and Biochemistry, Inorganic Chemistry I, Solid State Chemistry and Materials, Ruhr-Universität Bochum, D-44780 Bochum, Germany*

Received March 15, 2010

The most impressive feature of the crystal structure of $IrPr_6Cl_{11}$ is chains of face-sharing $\{Pr_6\}$ octahedra that encapsulate, alternatingly, iridium atoms and chloride ions, according to the formulation $\{(Ir,Cl)Pr_6\}Cl_{10}$. An alternative description of the structure is the connection of isolated $\{IrPr_6\}$ clusters that are surrounded in a mixed $\{ZR_6\}X^i_{12}/\{ZR_6\}X^i_8$ type by chlorido ligands with a rather complex connectivity, $\{IrPr_6\}(Cl^{i-a-a}_{4/3}Cl^{a-i-a}_{8/3}Cl^{i-a}_{6/2}Cl^{a-i}_{6/2})^e$-$(Cl^{i-i}_{2/2})^f$, to a three-dimensional structure of tetragonally packed cluster-complex chains.

Examples for isolated octahedral rare-earth-metal (R)/halide (X) cluster complexes are rare; none are known without an endohedral atom Z contributing its electrons for Z−R bonding. There is one almost ubiquitous structure type, especially for iodides, the $\{ZR_6\}X_{12}R$ type, in laboratory jargon also called the 7−12 type. A wide variety of endohedral possibilities have been collected, from both main-group and transition elements. At present, we count almost 100 examples, with $\{CSc_6\}I_{12}Sc$ belonging to the first examples for which it was recognized that an endohedral atom was needed.[1] They all contain the principal $\{ZR_6\}X^i_{12}X^a_6$ building units that are connected via i-a/a-i bridging according to $\{ZR_6\}X^i_6X^{i-a}_{6/2}$-$X^{a-i}_{6/2}R$, where a stands for terminal (μ_1) and i for *intra*cluster (μ_2) bridging ligands (over the edge of the R_6 octahedron); i−a and a−i denote *inter*cluster bridging.[2]

Further bridging leads to the $\{ZR_6\}X_{10}$ type. Compounds of that type almost exclusively crystallize with a structure first observed for $\{RuY_6\}I_{10}$,[3] for which the connectivities can be depicted as $\{ZR_6\}X_2^iX^{i-i}_{4/2}X^{i-a}_{6/2}X^{a-i}_{6/2}$. $\{FeLa_6\}Br_{10}$[4] and the new structurally different $\{IrPr_6\}Cl_{10}$[5] appear to be the only exceptions at present. In these, not only are edge-bridging halide ligands present, but there are also face-capping ligands. Thus, they may be described as being derived from a mixed $\{ZR_6\}X^i_{12}/\{ZR_6\}X^i_8$ type of cluster complex, which, of course, accounts for more diverse connectivities. Surprisingly enough, the endohedral atoms found so far for that structure type are almost exclusively transition-metal atoms from groups 8−10 with the exception of $\{(C_2)R_6\}I_{10}$ with R = La, Ce.[6] This may be interpreted in terms of the electron counts, with 14 and 16−18 electrons available for intracluster bonding with Z = C_2 and group 8−10 elements, respectively.

The intermediate formula type, $\{ZR_6\}X_{11}$, is rather elusive. There are only two examples in the literature: $\{(C_2)Sc_6\}I_{11}$[7] and $\{CoLa_6\}Cl_{11}$.[8] The former is based on less connections according to $\{(C_2)Sc_6\}I^i_4I^{i-i}_{2/2}I^{i-a}_{6/2}I^{a-i}_{6/2}$ and the latter is, again, a mixed $\{ZR_6\}X^i_{12}/\{ZR_6\}X^i_8$ type with rather complicated connections.

During recent attempts to gain more insight into the Z/Pr/X systems (with Z = group 8−10 elements; X = Cl, Br, I), we have not only observed $\{RuPr_3\}Cl_3$[9] and $\{IrPr_3\}I_3$ as well as $\{IrPr_6\}Cl_{10}$[5] but also $\{IrPr_6\}Cl_{11}$.[10−12] Unfortunately,

---

*To whom correspondence should be addressed. E-mail: gerd.meyer@uni-koeln.de. Web site: www.gerd.meyer.de.

(1) Hwu, S.-J.; Corbett, J. D. *J. Solid State Chem.* **1986**, *64*, 331.

(2) The nomenclature used throughout this communication is based on suggestions of Niggli, Schäfer, and Schnering and by one of the present authors. See: (a) Schäfer, H.; Schnering, H. G. *Angew. Chem.* **1964**, *76*, 833. (b) Meyer, G. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2729.

(3) Hughbanks, T.; Corbett, J. D. *Inorg. Chem.* **1989**, *28*, 631.

(4) Zheng, C.; Mattausch, Hj.; Hoch, C.; Simon, A. *Inorg. Chem.* **2008**, *47*, 2356.

(5) Herzmann, N. Dissertation, Universität zu Köln, Köln, Germany, 2009.

(6) Mattausch, Hj.; Hoch, C.; Simon, A. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1423.

(7) Dudis, D. S.; Corbett, J. D. *Inorg. Chem.* **1987**, *26*, 1933.

(8) Zheng, C.; Mattausch, Hj.; Hoch, C.; Simon, A. *J. Solid State Chem.* **2009**, *182*, 2307.

(9) Herzmann, N.; Mudring, A.-V.; Meyer, G. *Inorg. Chem.* **2008**, *47*, 7954.

(10) Synthesis: A mixture of 350 mg of $PrCl_3$ (synthesized via the ammonium chloride route and purified as described previously; see ref 11), 159.5 mg of Pr (Chempur, Karlsruhe, Germany, 99.9%), and 81.6 mg of Ir (Merck, Darmstadt, Germany, 99.9%) was filled in a tantalum tube, which was He-arc-sealed and jacketed with silica. The temperature program used was as follows: 1200 °C for 1 day, cooling at a rate of 2 °C/h to 700 °C, and annealing for 10 days and then to room temperature by turning off the power to the furnace. All manipulations were carried out under strict exclusion of air and especially moisture in a drybox (MBraun, Garching, Germany). Black fairly isotropic crystals in an approximately 90% yield (with PrOCl being the remaining 10%) were selected under a microscope in a drybox and sealed in thin-walled glass capillaries.

(11) (a) Meyer, G.; Ax, P. *Mater. Res. Bull.* **1982**, *17*, 1447. (b) Meyer, G. *Inorg. Synth.* **1989**, *25*, 146. (d) Meyer, G. In *Advances in the Synthesis and Reactivity of Solids*; Mallouk, T. E., Ed.; JAI Press: London, 1994; Vol. *2*, pp 1−26.

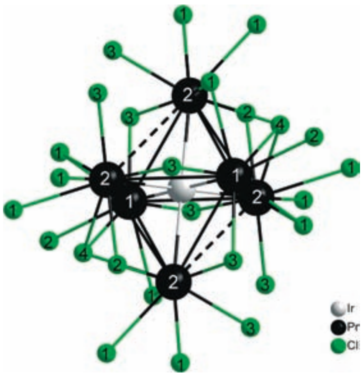

Figure 1. $\{IrPr_6\}$ octahedral cluster with its surrounding chloride ligands as it appears in $\{IrPr_6\}Cl_{11}$.

$\{IrPr_6\}Cl_{12}Pr$ was never seen, which would make the series complete, although the iodide $\{IrPr_6\}I_{12}Pr$ has been reported.[13]

The crystal structure of $\{IrPr_6\}Cl_{11}$ is rather unusual, although it can be understood formulawise as an intermediate between $\{IrPr_6\}Cl_{10}$ and $\{IrPr_6\}X_{12}Pr$. It is on the lower end of intracluster-based electrons, 16, as compared to 17 and 18 for the latter two. The $\{IrPr_6\}$ octahedron with the surrounding chloride ligands, as shown in Figure 1, is rather distorted. It shows an unusually large compression along the Pr1−Ir−Pr1 *pseudo*-4-fold axis (*pseudo* because the crystal system is monoclinic) with Ir−Pr1 distances of only 254.52(8) pm, as opposed to 303.01(6) pm for Ir−Pr2. Still the average of 287 pm lies in the usual range for Z−R distances in octahedral lanthanide clusters. This distortion affects also the intracluster angles, which deviate from 90° by almost ±9°; it also affects the Pr−Pr distances along the 12 edges of the octahedron, of which two are at 458.6(1) pm (see the broken lines in Figure 1); all of the others fall in a rather normal range around 395 pm. The distortion might be explained in the same manner as that for $\{FeLa_6\}Br_{10}$, with a 16-electron cluster as in the present case of $\{IrPr_6\}Cl_{11}$, by a Jahn−Teller-like stabilization, setting off the degeneracy of the t_{1u} levels.[4]

The $\{IrPr_6\}$ octahedron is surrounded by a total of 26 chloride ligands, with distances ranging from 285 to 307 pm. The connectivity is described by the following formulation: $\{IrPr_6\}(Cl^{i-a-a}{}_{4/3}Cl^{a-i-a}{}_{8/3}Cl^{i-a}{}_{6/2}Cl^{a-i}{}_{6/2})^e(Cl^{i-i}{}_{2/2})^f$, with e and f referring to edge and face capping of the chloride ligands with respect to the $\{IrPr_6\}$ octahedron. Hence, in $\{IrPr_6\}Cl_{11}$, the cluster is also of a mixed $\{ZR_6\}X^i{}_{12}/\{ZR_6\}X^i{}_8$ type. It is Cl4 that caps two triangular faces, although with distances of 287 (2×) and 307 pm, it is slightly off-center. Through the i−i ($\mu_3-\mu_3$) connection, it gains a coordination number of 6 and connects the cluster complexes, together with other bridgings, to a chain that is depicted in Figure 2.

Taking Ir−Pr distances of 255 and 303 pm (average of 287 pm) and Cl4−Pr distances of 287 and 307 pm (average of 300 pm) and the differences in size of the iridium and chlorine atoms into account, one could also interpret Cl4 as an endohedral atom occupying, alternating with iridium atoms, the centers of Pr_6 octahedra. Therefore, $\{IrPr_6\}Cl_{11}$ can also be written as $\{(Ir,Cl)Pr_6\}Cl_{10}$ with chains of face-sharing $\{ZPr_6\}$ octahedra with alternating endohedral atoms/ions Z = Ir, Cl. Although chlorine has an electron affinity considerably higher than that of iridium, that of the latter is by no means negligible. This is the reason why we have chosen to understand cluster complexes with electronegative endohedral atoms (main-group and transition-metal atoms alike) just as anti-Werner complexes.[2] In these, the central atom is an electronegative atom (Z = Ir and Cl in the present heteroendohedral case), which is surrounded in the first coordination sphere by electropositive atoms (R = Pr) and in the second coordination sphere by electronegative atoms (X = Cl). Bonding is of the polar covalent (Z−R) and rather ionic (R−X) types; see also ref 9.

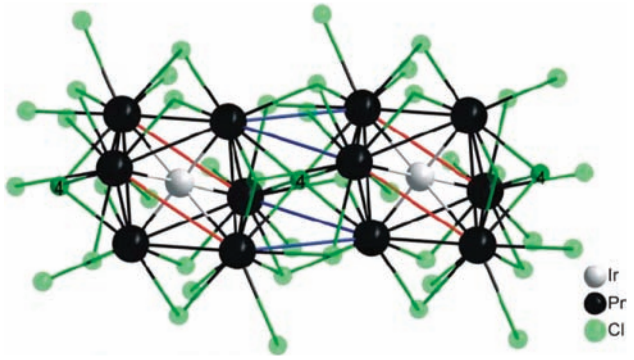

Figure 2. Connection of isolated $\{IrPr_6\}$ octahedral clusters via halide ligands, highlighting Cl4 with a coordination number of 6 in $\{(Ir,Cl)Pr_6\}Cl_{11}$.

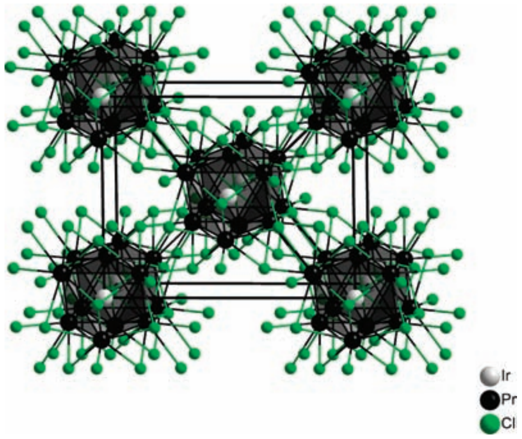

Figure 3. Nearly tetragonal packing of the cluster-complex chains and their connection via common halide bridges in the crystal structure of $\{(Ir,Cl)Pr_6\}Cl_{11}$.

The cluster-complex chains in $\{(Ir,Cl)Pr_6\}Cl_{11}$ are further connected via chloride bridging to neighboring chains. Packing of the chains parallel [001] is of the (somewhat compressed) tetragonal type, as shown in Figure 3.

In conclusion, with $\{IrPr_6\}Cl_{11}$, or better $\{(Ir,Cl)Pr_6\}Cl_{10}$, we have found an additional example for the still-rare class of mixed $\{ZR_6\}X^i{}_{12}/\{ZR_6\}X^i{}_8$ type cluster complexes. It is only the third such example for the $\{ZR_6\}X_{10}$ formula type, with the other two being $\{FeLa_6\}Br_{10}$[4] and $\{IrPr_6\}Cl_{10}$.[5] It features chains of cluster complexes with $\{IrPr_6\}$ octahedra isolated and connected via i−a bridging and with one i−i bridging chloride of coordination number 6, centering a Pr_6 octahedron. Therefore, an alternative description of the

---

[12] Crystal data for $\{IrPr_6\}Cl_{11}$: monoclinic, space group *C*2/*m* (No. 12); $a = 1032.6(2)$ pm, $b = 1273.5(3)$ pm, $c = 731.85(16)$ pm, $\beta = 94.705°$, $V = 959.2(4) \times 10^6$ pm^3; $Z = 2$; $5.19 < \theta < 55.52$; Mo Kα radiation (graphite monochromator, $\lambda = 71.073$ pm); $T = 293(2)$ K; $F(000) = 1236$; $\mu = 23.345$ mm^{-1}; 20 228 reflections measured, 3716 unique, 1188 observed. $R_{int} = 0.0511$, R1/wR2 = 0.0260/0.0469 [$I_0 > 2\sigma(I_0)$] and 0.0396/0.0490 [all data]; GOF on F^2 = 0.904.

[13] Payne, W.; Corbett, J. D. *Inorg. Chem.* **1990**, *29*, 2246.

structure is chains of face-sharing octahedra centered by alternating iridium and chlorine atoms, according to the formulation $\{(Cl,Ir)Pr_6\}Cl_{10}$.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft in the framework of Sonderforschungsbereich 608 (complex transition-metal compounds with charge and orbital degrees of freedom and disorder) as well as by direct sources from Universität zu Köln.

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.