

Communication

## Ru<sub>11</sub>Lu<sub>20</sub>, a New Intermetallic Compound with Eight- to Ten-Coordinate Ruthenium Atoms

Sina Zimmermann, Ingo Pantenburg and Gerd Meyer \*

Department für Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Germany;

E-Mails: sina.babai@googlemail.com (S.Z.); ac118@uni-koeln.de (I.P.)

\* Author to whom correspondence should be addressed; E-Mail: gerd.meyer@uni-koeln.de;  
Tel.: +49-221-470-3262; Fax: +49-221-470-5083.

Received: 14 May 2012; in revised form: 11 June 2012 / Accepted: 12 June 2012 /

Published: 20 June 2012

---

**Abstract:** The new intermetallic compound Ru<sub>11</sub>Lu<sub>20</sub> was obtained as black single crystals during an attempted comproportionation reaction of lutetium(III) chloride, LuCl<sub>3</sub>, with metallic lutetium in the presence of ruthenium metal at 950 °C. Ru<sub>11</sub>Lu<sub>20</sub> crystallizes with the trigonal space group *R*-3, *Z* = 6, *a* = 1255.1(1), *c* = 2973.0(4) pm, *R*<sub>1</sub> for all data: 0.0380. Ruthenium atoms center eight-, nine- and ten-vertex polyhedra of lutetium atoms which are connected in a complicated manner to a three-dimensional network.

**Keywords:** ruthenium; lutetium; polar intermetallic; crystal structure

---

### 1. Introduction

A plethora of reduced rare-earth metal halides at the borderline between metal and salt have been obtained within the last decades [1–12]. These contain cluster complexes, most frequently of the “6–12” type, in which octahedral metal clusters {R<sub>6</sub>} are surrounded by twelve halide ligands (X) capping all the edges. As the rare-earth elements R contribute only three valence electrons to intra-cluster bonding, an endohedral atom Z is needed to stabilize the cluster {ZR<sub>6</sub>} through R—Z polar covalent bonding interactions.

Rare-earth cluster complexes with endohedral atoms, {ZR<sub>x</sub>}X<sub>z</sub>, may be obtained by comproportionation reactions of the respective rare-earth trichloride, RX<sub>3</sub>, with the metals R and Z. During one of the many attempts to synthesize new lutetium cluster complexes, in the present case in

the system LuCl<sub>3</sub>/Lu/Ru, the new intermetallic compound {Ru<sub>11</sub>Lu<sub>20</sub>} was obtained as black single crystals.

## 2. Results and Discussion

The analysis of single-crystal X-ray diffraction data of the small black crystals obtained during an attempt to synthesize {RuLu<sub>6</sub>}Cl<sub>12</sub>Lu—in analogy to {ZSc<sub>6</sub>}Cl<sub>12</sub>Sc compounds which exist at least with Z = Co, Ni [13]—revealed the new intermetallic phase {Ru<sub>11</sub>Lu<sub>20</sub>}. This composition was not reported in the phase diagram of the binary system Ru/Lu [14]. The phase that comes closest is Ru<sub>3</sub>Lu<sub>5</sub>, with 37.5 mol% Ru, as compared with 35.48 mol% in {Ru<sub>11</sub>Lu<sub>20</sub>}. “Ru<sub>3</sub>Lu<sub>5</sub>” melts incongruently at 1460 °C: As crystallographic data are not reported it seems likely that “Ru<sub>3</sub>Lu<sub>5</sub>” = “Ru<sub>12</sub>Lu<sub>20</sub>” is in fact {Ru<sub>11</sub>Lu<sub>20</sub>}.

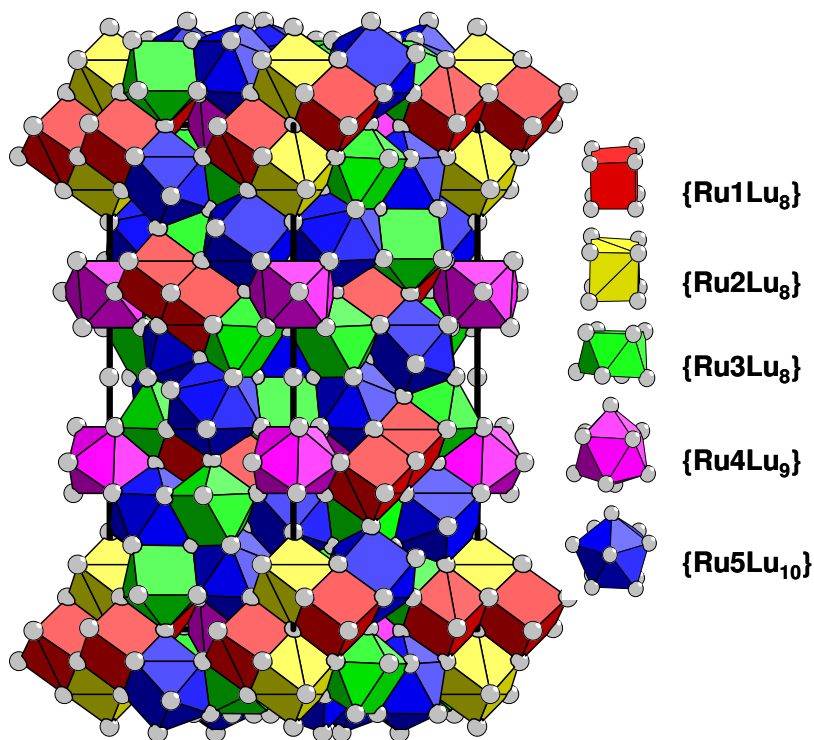
The crystal structure of {Ru<sub>11</sub>Lu<sub>20</sub>} exhibits a large unit cell, space group *R*-3, in the hexagonal setting with  $a = 1255.1(1)$ ,  $c = 2973.0(4)$  pm, with six formula units in the unit cell, hence with the composition Ru<sub>66</sub>Lu<sub>120</sub>. There are five crystallographically independent ruthenium sites in the unit cell, Wyckoff notations 6*c* (Ru2, Ru4) and 18*f* (Ru1, Ru3, Ru5), and nine lutetium sites at 3*a* (Lu1), 3*b* (Lu9), 6*c* (Lu8), and 18*f* (Lu2–Lu7).

As the electron affinity of ruthenium is higher than that of lutetium, 101 vs. 33 kJ/mol [15,16], {Ru<sub>11</sub>Lu<sub>20</sub>} could be regarded as a polar intermetallic compound. The sequence of the atoms, more negative to more positive in the waved brackets, is used in analogy to anti-Werner cluster complexes [12]. These are compounds of the general formula {ZR<sub>*x*</sub>}X<sub>*z*</sub>, in which a central (transition) metal atom Z, for example Ru, is surrounded by *x* R metal atoms, for example Lu, and further, in the second coordination sphere, by *z* X atoms, usually halogen atoms, such that the polarities are  $-(Z)$ ,  $+(R)$ ,  $-(X)$ . Although {Ru<sub>5</sub>Lu<sub>20</sub>}I<sub>24</sub> was clearly shown to exist by powder X-ray diffraction data, the crystals were much too thin to determine the details of the crystal structure [17]. However, the compound is isostructural with {Os<sub>5</sub>Lu<sub>20</sub>}I<sub>24</sub> whose structure could be established by single crystal X-ray diffraction data [18]. Essential features are chains of face-sharing {OsLu<sub>8</sub>} cubes and square antiprisms in a 1:4 ratio. These {OsLu<sub>8/2</sub>} → {Os<sub>5</sub>Lu<sub>20</sub>} chains constitute a one-dimensional intermetallic “phase” which is surrounded by iodide ligands in the second coordination sphere. Heteroatomic Os–Lu distances are, on the average, 293.2 pm (cube) and 281.7 pm (square antiprisms), hence considerably shorter than homoatomic Lu–Lu distances of 343.3 pm (average over all relevant Lu–Lu distances) and Os–Os distances of 298.8(1), 302.9(1), and 325.0(1) pm, respectively.

In the new polar intermetallic compound {Ru<sub>11</sub>Lu<sub>20</sub>} there are three crystallographically independent {RuLu<sub>8</sub>} polyhedra, two of which may be regarded as cubes (surrounding Ru1 and Ru2) and one as a square antiprism (around Ru3); the {Ru4Lu<sub>9</sub>} and {Ru5Lu<sub>10</sub>} polyhedra are best described as a monocapped square antiprism (1-4-4) and a 1-5-4 polyhedron, see Figure 1. These polyhedra occur in a 3:1:3:1:3 ratio, hence seven ruthenium atoms out of eleven, in {Ru<sub>11</sub>Lu<sub>20</sub>}, have coordination number eight (CN = 8), one has CN = 9, and three have CN = 10. All heteroatomic, polar Ru–Lu distances are shorter than the shortest homoatomic Lu–Lu or Ru–Ru distances, Table 1. In numbers, Ru–Lu distances range from 284.4 to 307.5 pm, with an overall average of 292.4 pm; the shortest Lu–Lu distances range from 319.8(1) to 358.6(1) pm with an average of 325.2 pm, and the

shortest Ru–Ru distance is 328.3(1) pm (Ru1–Ru3). These values are all very similar to those observed in  $\{\text{Os}_5\text{Lu}_{20}\}\text{I}_{24}$ , see above.

**Figure 1.** A  $[1-10]$  projection of the crystal structure of  $\{\text{Ru}_{11}\text{Lu}_{20}\}$ . The colors represent the five crystallographically independent  $\{\text{RuLu}_x\}$  polyhedra, with  $x = 8, 9,$  and  $10$ , see right part of the Figure.



**Table 1.** Ru–Lu and Ru–Ru distances in the crystal structure of  $\{\text{Ru}_{11}\text{Lu}_{20}\}$ .

Z–R	CN	d/pm; Range	d/pm; Average	Z–Z	d/pm; Shortest
Ru1–Lu	8	279.2(2)–292.5(2)	284.9	Ru1–Ru	328.3(2)
Ru2–Lu	8	277.0(3)–294.5(3)	284.4	Ru2–Ru	340.2(2)
Ru3–Lu	8	271.5(2)–309.0(2)	285.8	Ru3–Ru	328.3(2)
Ru4–Lu	9	292.4(2)–302.3(1)	297.1	Ru4–Ru	417.6(2)
Ru5–Lu	10	285.4(2)–336.6(2)	307.5	Ru5–Ru	353.9(2)

Given that the analogy between the three-dimensional polar intermetallic compound  $\{\text{Ru}_{11}\text{Lu}_{20}\}$  and the one-dimensional polar intermetallic incorporated as a cluster chain in the anti-Werner cluster complex  $\{\text{Ru}_5\text{Lu}_{20}\}\text{I}_{24}$  is accepted, the crystal structure of  $\{\text{Ru}_{11}\text{Lu}_{20}\}$  may be described as a connection between seven  $\{\text{RuLu}_8\}$  (cube and square antiprism in a 4:3 ratio), one 1-4-4  $\{\text{RuLu}_9\}$  and three 1-5-4  $\{\text{RuLu}_{10}\}$  polyhedra. As Figure 1 shows, the connection between these polyhedra is surprisingly complex.

### 3. Experimental Section

Anhydrous lutetium trichloride,  $\text{LuCl}_3$ , was prepared following the ammonium-chloride route [19] and purified by high-vacuum sublimation at around 900 °C. Lutetium and ruthenium metals were from Smart Elements and Merck, respectively. A mixture of 150 mg  $\text{LuCl}_3$  (0.533 mmol), 70 mg lutetium (0.400 mmol) and 24 mg ruthenium (0.237 mmol) was filled under dry-box conditions (argon, MBraun, Garching, Germany) in pre-cleaned and at one end He-arc welded tantalum containers. These were then sealed at the other end and jacketed under vacuum in silica ampoules. The reaction ensemble was heated with a rate of 10 K/h to 950 °C, kept there for two weeks and then cooled to ambient temperature with 10 K/h.

The reaction products were inspected under a microscope. The small black crystals within white crystalline materials turned out to be the intermetallic phase  $\text{Ru}_{11}\text{Lu}_{20}$ . Single crystals were selected under a microscope and mounted in thin-walled glass capillaries. This was unnecessary although before structure determination a lutetium chloride cluster complex was expected, and these are sensitive to moisture.

The quality of the crystals was checked on a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS II), and a complete intensity data set was collected at ambient temperature using graphite-monochromated Mo- $\text{K}_\alpha$  radiation. The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data; the programs used in this work are Stoe's X-Area, including X-RED and X-SHAPE for data reduction and absorption correction [20,21]. The WinGX suite of programs [22], including SIR-92 [23] and the SHELX programs [24–26] were used for structure solution and refinement. The last refinement cycles included atomic positions for all atoms and anisotropic thermal parameters. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; E-Mail: crysdata@fizkarlsruhe.de), on quoting the depository number ICSD-424634 the authors and the journal citation.

Crystal data for  $\text{Ru}_{11}\text{Lu}_{20}$ , 4611.17  $\text{g}\cdot\text{mol}^{-1}$ ; diffractometer IPDS-II, Stoe, Darmstadt, Germany; Mo- $\text{K}_\alpha$  (graphite monochromator,  $\lambda = 71.073$  pm);  $T = 298(2)$  K;  $2\theta_{\text{max}} = 54.8^\circ$ ;  $0^\circ \leq \omega \leq 180^\circ$ ,  $\varphi = 0^\circ$ ,  $0^\circ \leq \omega \leq 158^\circ$ ,  $\varphi = 90^\circ$ ,  $\Delta\omega = 2^\circ$ , 169 images;  $-16 \leq h \leq 16$ ,  $-16 \leq k \leq 15$ ,  $-38 \leq l \leq 38$ ;  $\rho_{\text{calc}} = 11.327$   $\text{g}\cdot\text{cm}^{-3}$ ; 10990 measured reflections of which 2012 were symmetrically independent;  $R_{\text{int}} = 0.1018$ ;  $F(000) = 11424$ ;  $\mu = 78.110$   $\text{mm}^{-1}$ . Trigonal,  $R\bar{3}$  (no. 148),  $a = 1255.1(1)$ ,  $c = 2973.0(4)$  pm,  $V = 4056.1(7) \times 10^6$   $\text{pm}^3$ ,  $Z = 6$ ;  $R$  values:  $R_1/wR_2$  for 1356 reflections with  $[I_0 > 2\sigma(I_0)]$ : 0.0364/0.0786, for all data: 0.0630/0.0855;  $S_{\text{all}} = 0.884$ ;  $\Delta\rho$  (min./max.) =  $-2.48/2.78 \times 10^{-6}$   $\text{pm}^{-3}$ .

### 4. Conclusions

The hitherto unknown intermetallic compound  $\{\text{Ru}_{11}\text{Lu}_{20}\}$ —perhaps identical with “ $\text{Ru}_3\text{Lu}_5$ ” as reported in a phase diagram determination—consists of central ruthenium atoms coordinated by eight (cube, square antiprism), nine (monocapped square antiprism, 1-4-4) and ten (1-5-4 polyhedron) lutetium atoms. These polyhedra are connected to a complicated three-dimensional structure. Coordination numbers of eight (cube and square antiprisms) are also observed in the cluster complex

compound  $\{\text{Ru}_5\text{Lu}_{20}\}\text{I}_{24}$  where the polyhedra are connected via common faces to a one-dimensional intermetallic structure; the chains are isolated from each other by surrounding iodide ligands.

### Acknowledgements

This work was generously supported by the State of Nordrhein-Westfalen through the Universität zu Köln.

### References

1. Corbett, J.D. Extended metal-metal bonding in halides of the early transition metals. *Acc. Chem. Res.* **1981**, *14*, 239–246.
2. Simon, A. Condensed metal clusters. *Angew. Chem. Int. Ed.* **1981**, *20*, 1–22.
3. Meyer, G. Reduced halides of the rare-earth elements. *Chem. Rev.* **1988**, *88*, 93–107.
4. Simon, A. Extended metal-metal bonding in halides of the early transition metals. *Angew. Chem. Int. Ed.* **1988**, *27*, 159–183.
5. Corbett, J.D. Exploratory synthesis in the solid state. Endless Wonders. *Inorg. Chem.* **2000**, *39*, 5178–5191.
6. Corbett, J.D. Exploratory synthesis of reduced rare-earth-metal halides, chalcogenides, intermetallics: New compounds, structures, and properties. *J. Alloys Compd.* **2006**, *418*, 1–20.
7. Corbett, J.D. The fascinating and diverse chemistry of polar intermetallic phases. *Inorg. Chem.* **2010**, *49*, 13–28.
8. Simon, A.; Mattausch, H.J.; Miller, G.J.; Bauhofer, W.; Kremer, R.K. Chapter 100 Metal-Rich Halides–Structure, Bonding and Properties. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K.A., Eyring, L., Eds.; Elsevier Science: Amsterdam, Netherlands, 1991; Volume 15, pp. 191–285.
9. Meyer, G.; Wickleder, M.S. Simple and Complex Halides. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K.A., Eyring, L., Eds.; Elsevier Science: Amsterdam, Netherlands, 2000; Volume 28, Chapter 177, pp. 53–129.
10. Simon, A.; Mattausch, H.J.; Ryazanov, M.; Kremer, R.K. Lanthanides as d Metals. *Z. Anorg. Allg. Chem.* **2006**, *632*, 919–929.
11. Meyer, G. The reduction of rare-earth metal halides with unlike Metals–Wöhler’s metallothermic reduction. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2537–2552.
12. Meyer, G. Cluster complexes as anti-Werner complexes. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2729–2736.
13. Zimmermann, S. Hochkoordinierte endohedrale Übergangsmetallatome in Scandiumclustern. Ph.D. Thesis, Universität zu Köln, Köln, Germany, 2008.
14. Okamoto, H. Lu-Ru Phase Diagram. In *ASM Alloy Phase Diagram Center*; Villars, P., Okamoto, H., Cenzual, K., Eds.; ASM International, Materials Park: OH, USA, 2006; diagram No. 901545.
15. Norquist, P.L.; Beck, D.R.; Bilodeau, R.C.; Scheer, M.; Srawley, R.A.; Haugen, H.K. Theoretical and experimental binding energies for the  $d^7s^2\ ^4F$  levels in  $\text{Ru}^-$ , including calculated hyperfine structure and  $M1$  decay rates. *Phys. Rev. A* **1999**, *59*, 1896–1902.

16. Davis, V.T.; Thompson, J.S. Measurement of the electron affinity of lutetium. *J. Phys. B: At. Mol. Opt. Phys.* **2001**, *34*, L433–L437.
17. Brühmann, M. Cluster-Komplexe der Seltenerdmetalle Gadolinium und Lutetium mit endohedralen Übergangsmetall-Atomen. Ph.D. Thesis, Universität zu Köln, Köln, Germany, 2011.
18. Brühmann, M.; Mudring, A.-V.; Valldor, M.; Meyer, G.  $\{\text{Os}_5\text{Lu}_{20}\}\text{I}_{24}$ , the first extended cluster complex of Lutetium with eight-coordinate endohedral Osmium atoms in two different environments. *Eur. J. Inorg. Chem.* **2011**, 4083–4088.
19. Meyer, G. The ammonium chloride route to anhydrous rare earth chlorides—The example of  $\text{YCl}_3$ . *Inorg. Syntheses* **1989**, *25*, 146–150.
20. *X-RED 1.22, Stoe Data Reduction Program (C)*; Stoe & Cie GmbH: Darmstadt, Germany, 1999.
21. *X-Shape 1.06, Crystal Optimisation for Numerical Absorption Correction (C)*; Stoe & Cie GmbH: Darmstadt, Germany, 1999.
22. Farrugia, L.J. *WINGX, A MS-Windows System of Programs for Solving, Refining and Analysing Single X-ray Diffraction Data for Small Molecules*; University of Glasgow: Glasgow, Scotland, 2005.
23. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gualardi, A. SIR92, a program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **1993**, *26*, 343–350.
24. Sheldrick, G.M. A short history of *SHELX*. *Acta Cryst.* **2008**, *A64*, 112–122.
25. Sheldrick, G.M. *SHELXS-97, Program for Structure Analysis*; University of Göttingen: Göttingen, Germany, 1998.
26. Sheldrick, G.M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

© 2012 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).