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An Alternative Description of the Structures of Rh_7Mg_{44} and Mg_6Pd

By Sten Andersson

Inorganic Chemistry II, *Chemical Center, Lund, Sweden*

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The structure types of Rh_7Mg_{44} and Mg_6Pd are described by means of packing octahedra and tetrahedra. The host structure common to the two types is a cubic intergrowth of two different building units. One unit has the Mg atoms arranged as the anions in Keggin's ion ($PW_{12}O_{40}^{3-}$), and the other is an octahedrally capped block of the pyrochlore structure.

Experience has shown that when structures are described and related to each other and to crystal properties, it is invaluable to have an idealized model. A model of regular polyhedra should easily transform into the real structure by very small topological distortions and *vice versa* (Hyde, Bursill, O'Keeffe & Andersson, 1972). The icosahedral method of representing structures lacks this fundamental property, of course, and this is the reason why we search for different methods of describing some structures.

The general approach is the following: polyhedra of groups of fused polyhedra, containing five-membered rings of atoms, are created in structures by or between units of regular polyhedra or groups of regular polyhedra. Our confidence in this approach has grown, and it was tempting to try to dissect an intermetallic compound with a so-called giant cell along these lines.

Rh_7Mg_{44}

Recently we described the structure of $Mg_3Cr_2Al_{18}$ as being built from nearly regular pyrochlore units and Friauf polyhedra (Nyman, Andersson, Hyde & O'Keeffe, 1978). Such a pyrochlore unit consists of a central octahedron sharing every second face with four other octahedra. It was shown how two pyrochlore units cooperate in the structure to create an icosahedron, distorted exactly as it is in the real structure. The ideal structure, with regular octahedra and truncated tetrahedra, was shown to deviate very little from the real structure.

Westin & Edshammar (1971, 1972*a*,*b*) reported the structures of the isostructural compounds Rh_7Mg_{44}, Ru_7Mg_{44} and Ir_7Mg_{44}. Samson & Hansen (1972) reported on the structure of Na_6Tl and Mg_6Pd, two similar but not identical structures. Westin & Edshammar pointed out that Na_6Tl was isostructural with their group of compounds.

Rh_7Mg_{44} is cubic, $a = 20{\cdot}148$ Å, $F\bar{4}3m$. Westin & Edshammar (1971) describe the structure as built up of icosahedral complexes of three kinds. One complex has six icosahedra sharing faces, one has four sharing faces, as in γ-brass, and finally, four icosahedra share corners as in VAl_{10} or $Mg_3Cr_2Al_{18}$. Additional Mg(10) atoms form isolated tetrahedra in this structural description.

In Samson's (1972) description of the same structure type, he uses complexes of 14 icosahedra and 42 centred pentagonal prisms, and a Friauf polyhedron is shared between four such complexes.

After projecting the atoms of Rh_7Mg_{44} along the cubic axis, it was obvious that the structure was rich in octahedral and tetrahedral interstices (Fig. 1). Certain familiar groupings of octahedra were recognized, and a

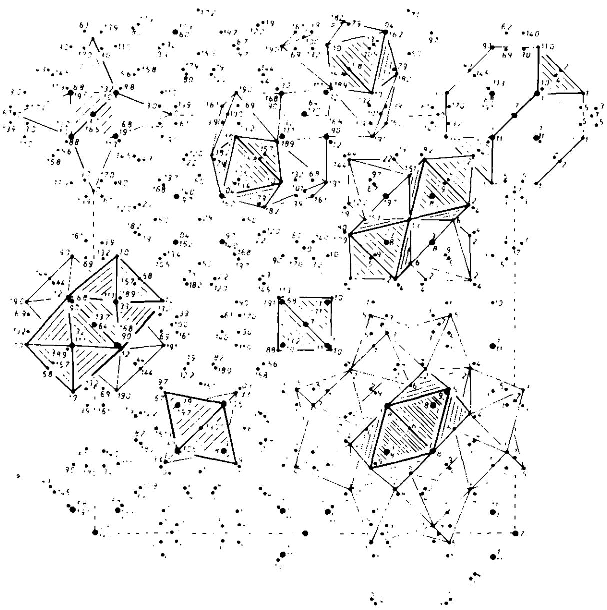

Fig. 1. Rh_7Mg_{44} projected along a cube axis. Rh atoms are excluded. Larger circles are two exactly overlapping Mg atoms. On one side of a mirror plane the heights of atoms are given in Ångström units and decimal fractions. On the other side only identification numbers of atoms are given. The unit cell is indicated by dotted lines. For explanation of various polyhedral units, see the text.

Table 1. *Comparison of the observed parameters of* Rh_7Mg_{44}, Ru_7Mg_{44}, Ir_7Mg_{44}, Na_6Tl (*averaged*), Mg_6Pd *and calculated parameters from the model of Fig.* 2

The deviations that occur between observed parameters of isostructural compounds are given within brackets.

	Observed (Rh, Ru, Ir and Na_6Tl)		Observed (Mg_6Pd)		Calculated	
	x	z	x	z	x	z
Mg(1)	0·0521 (0·0016)	0·3387 (0·0022)	0·049	0·3428	0·0539	0·3383
Mg(2)	0·1075 (0·0018)	0·2158 (0·0037)	0·1065	0·2160	0·1060	0·2159
Mg(3)	0·1940 (0·0021)	0·4807 (0·0016)	0·1934	0·4824	0·1961	0·4820
Mg(4)	0·0992 (0·0098)	0·7194 (0·0051)	0·0990	0·7219	0·0900	0·6977
Mg(5)	0·1581 (0·0041)	0·9798 (0·0043)	0·1560	0·9761	0·1619	0·9740
Mg(6)		0·3565 (0·0033)		0·3572		0·3500
Mg(7)		0·1825 (0·0029)		0·1858		0·1820
Mg(8)	0·6980 (0·0113)		missing		0·6961	
Mg(9)	0·8333 (0·0033)		0·8496		0·8398	
Mg(10)	0·5653 (0·0159)		0·5813		0·5539	
Mg(11)	0·9478 (0·0011)		0·9475		0·9460	

model of the structure was constructed with regular octahedra. Fig. 2 gives a colour picture of the model built, and the red unit of octahedra is simply the Keggin polyion, $PW_{12}O_{40}^{3-}$, with Mg replacing the O atoms at the octahedral corners. The blue unit can easily be derived from a pyrochlore unit by octahedral capping (Fig. 3). The pyrochlore unit is somewhat compressed by the regular blue octahedra in the figure. The pyrochlore unit is shown in the middle right part of Fig. 1, and its capping is shown below in Fig. 1 (blue unit in Fig. 2).

From the regular units of the red Keggin ion and the blue, octahedrally capped pyrochlore unit, the unit-cell dimension of this structure type can be calculated by simple trigonometry: $a(\text{calc}) = 6{\cdot}5575 O_e$, where O_e is the Mg–Mg distance in a regular octahedron (octahedral edge). If O_e is 3·06 Å, a(calc) becomes 20·13 Å. Westin & Edshammar noted that in spite of the differences in metallic radii between the elements of the different isostructural compounds they all have almost identical unit-cell dimensions, and they suggested that the electronic structure may affect the cell volume. However from Fig. 2 it is obvious that the structure is built up of a rigid skeleton of simple building block units, which keep the unit-cell dimensions intact. Geometrically, this is analogous to zeolite crystal chemistry.

The rigid skeleton of Fig. 2, is common for the Rh_7Mg_{44} group of compounds, as well as the $PdMg_6$ alloy. The red Keggin unit contains various structural features. Inside the unit, there is a truncated tetrahedron (c.c.p.)*, which is shown in the right-hand top corner of Fig. 1. If each of the hexagonal faces is capped with three edge-sharing octahedra (partly shown on Fig. 1, to the left of the truncated tetrahedron) the Keggin unit is obtained. The truncated tetrahedron can also be described by means of four edge-sharing octahedra (c.c.p.), as is shown in the left middle part of Fig. 1. This grouping of octahedra has a central tetrahedron Mg(10), and if this is expanded uniformly, the truncated tetrahedron turns into a Friauf polyhedron. The expansion of the tetrahedron also pushes the atoms Mg(4) out, and this rather small topological distortion can be studied in Fig. 1. It is a natural distortion when the Friauf polyhedron is centred, as it is in Mg_6Pd. But this is not the case in Rh_7Mg_{44} and it might be that here, in order to make the icosahedron around Rh(1) (see below) less irregular, the Mg(4) and Mg(10) atoms are pulled out from the truncated tetrahedron. This cooperative tendency in the structure to turn the truncated tetrahedron into a Friauf polyhedron and make the icosahedra more regular, is the only significant distortion from the ideal regular structure shown in Fig. 2. This becomes obvious when the parameters are calculated assuming regular octahedra and tetrahedra, as shown in Table 1, where they are compared with observed parameters.

The Keggin unit can also be described as four fused pyrochlore units, and also as four fused twinned cuboctahedra (h.c.p.). The octahedral capping of the pyrochlore unit (blue in Fig. 2) also contains many pentagonal prisms, a polyhedron used by Samson (1972) in his description of Na_6Tl and Mg_6Pd.

We have earlier shown how ideal octahedral units generate icosahedra, and it is remarkable how the regular skeleton of Fig. 2 generates the icosahedral groups of four and six icosahedra containing Rh(1), Rh(2) and Rh(3) in Rh_7Mg_{44}. Rh(3) is easily formed by corner sharing between the blue and the red unit of Fig. 2. The generation of this icosahedron is identical with the one occurring in $Mg_3Cr_2Al_{18}(VAl_{10})$. One pyrochlore piece of the Keggin unit and the octahedrally capped pyrochlore unit form the icosahedron (Fig. 3). Here it is also shown how four icosahedra share corners through the pyrochlore unit. In the blue–red skeleton of Fig. 2 there are now two different, rather

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* Here we define a truncated tetrahedron as c.c.p., with atoms centring the hexagonal faces. When these four atoms are pulled out to cap the large tetrahedron, a Friauf polyhedron is obtained.

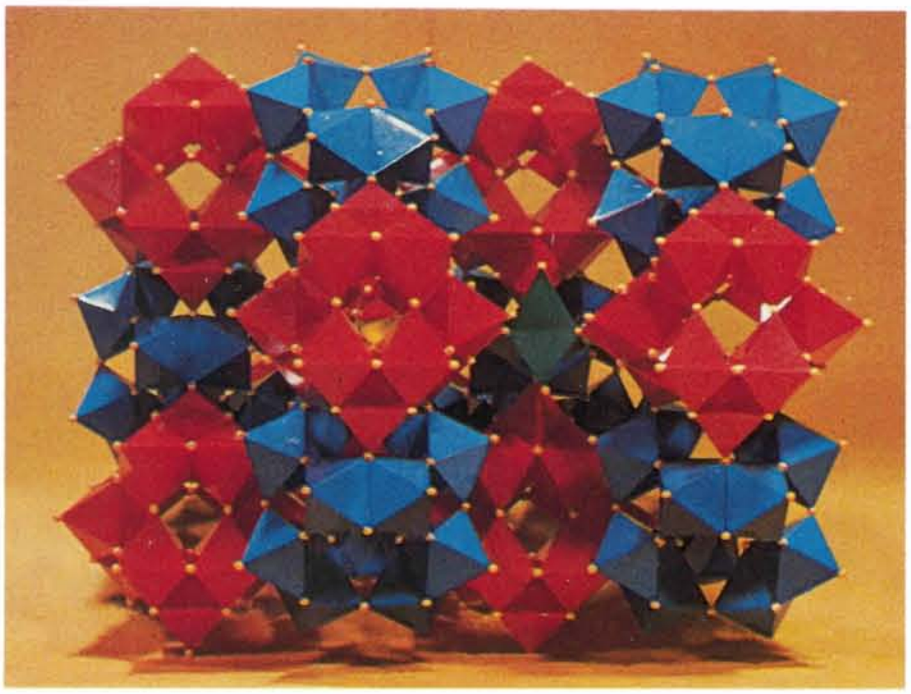

Fig. 2. Polyhedral model of Rh_7Mg_{44}. For the deviations between this ideal model and the real structure, see Table 1.

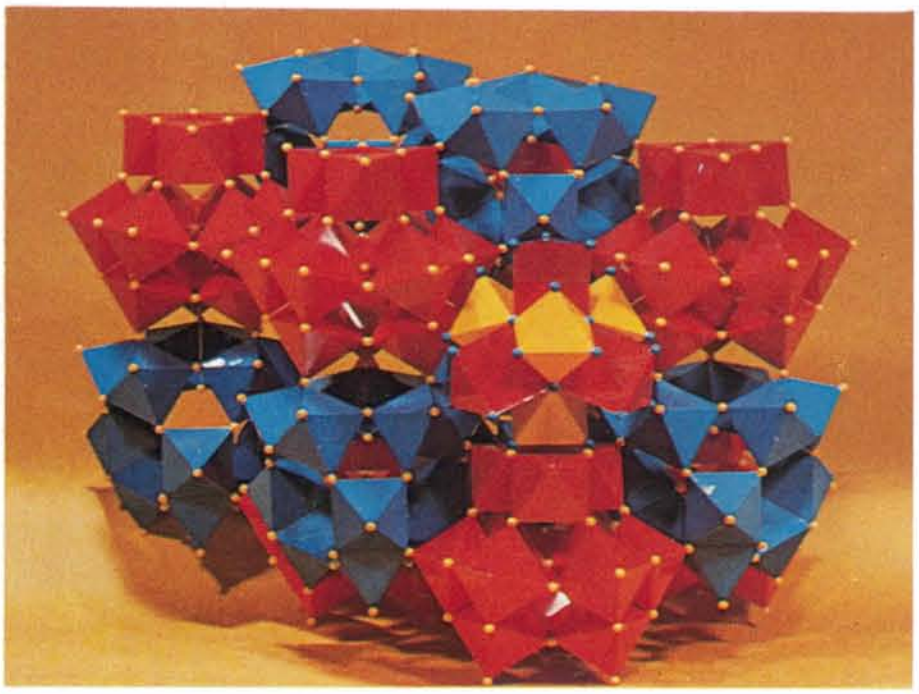

Fig. 4. U_2F_9 unit of trigonal prisms and octahedra in Mg_6Pd, substituting for the six-icosahedron complex in Rh_7Mg_{44}. The U_2F_9 unit is somewhat too small, blue balls should be substituted for yellow balls. The arrangement of octahedra in the U_2F_9 is again a pyrochlore unit.

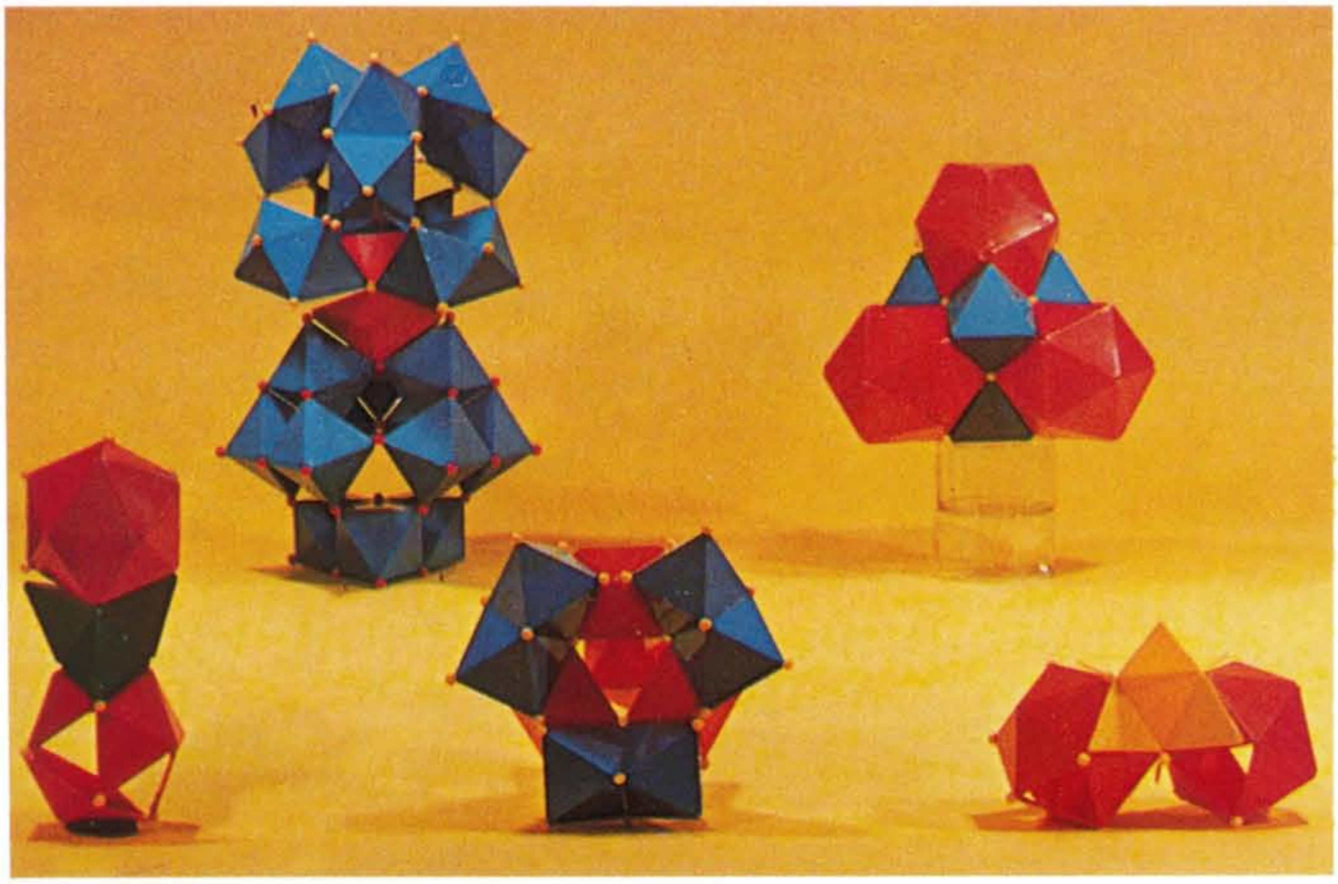

Fig. 3. (Upper left corner) Keggin unit (blue here, but red in Fig. 2) and the blue octahedrally capped pyrochlore unit form an icosahedron (red), Rh(3). (Upper right corner) Four icosahedra [Rh(3)] sharing corners, partly generated by the blue central pyrochlore unit. The rest of the icosahedral corners are generated by four Keggin units as in the left model. (Lower left corner) The green unit, composed of five face-sharing tetrahedra, generates the six-icosahedron complex [Rh(1)], of which only two red icosahedra are shown. (Lower right corner) The yellow unit of a tetrahedron capped by four triangles, generates the four-icosahedron complex [Rh(2)], of which only two red icosahedra are shown. (Lower centre) Pyrochlore unit, partly capped by octahedra, to give the blue unit of Fig. 2.

large, empty cages. One is filled by a complex of six face-sharing icosahedra, containing Rh(1) shown in Fig. 3, and surrounding a green unit, composed of five tetrahedra sharing faces. This green unit, visible in Fig. 2, generates, together with the general skeleton, and with four tetrahedra sitting on four Keggin units, all the atoms needed for the complex of six face-sharing icosahedra. The regularity of the five-tetrahedron unit can be studied in the lower left part of Fig. 1.

The yellow, triangle-capped tetrahedron, visible in Figs. 2 and 3, generates the complex of four face-sharing icosahedra with Rh(2). Again, this yellow unit and the octahedral skeleton, generates all the atoms necessary to form this icosahedral complex. The yellow unit is also shown in Fig. 1, upper left corner.

Mg_6Pd

The main difference between the structure of Rh_7Mg_{44} and Mg_6Pd seems to be that Mg(8) of Rh_7Mg_{44} is missing in Mg_6Pd, and also that Rh(1) is substituted for one Mg, *viz.* Mg(7), in Mg_6Pd. In that way a regular octahedron of Mg is formed. However, the edge of this octahedron is rather large: 3·37 compared with 3·05 Å for the octahedron formed by Mg(6). This Mg(7) octahedron substitutes for the green five-tetrahedron unit, which partly generated six icosahedra. This Mg(7) octahedron is surrounded by four face-sharing octahedra exactly as Mg(6), forming again the well-known pyrochlore unit. The additional Mg atoms of these face-sharing octahedra forming the pyrochlore unit are provided by the Keggin unit of the skeleton. Furthermore, the blue unit in the skeleton provides more atoms to form four trigonal prisms sharing faces with the Mg(7) central octahedron. The complete unit that substitutes for the six-icosahedron complex in the large cavity of Rh_7Mg_{44} and $PdMg_6$ is thus a central octahedron sharing faces with four octahedra and four trigonal prisms (Fig. 4). An identical arrangement of atoms is present in the structure of U_2F_9, the trigonal prisms being centred by U atoms and the octahedra empty (Nyman, 1978). In Fig. 4 an ideal unit of this kind is fitted into the common skeleton of Mg_6Pd and Rh_7Mg_{44}. The ideal unit here is obviously too small, and this is the reason why the central Mg(7) octahedron is unusually large.

This U_2F_9 unit was described by Westin (1972) as consisting of four tri-capped trigonal prism polyhedra sharing faces. Instead, trigonal prisms share only corners in the structure of Mg_6Pd, as also was described by Samson (1972).

Final remarks

Mg_6Pd and Rh_7Mg_{44} form the same skeleton of Mg atoms as shown by the blue and red units in Fig. 2. This skeleton forms two large cavities, which in Rh_7Mg_{44} are filled by four-icosahedron complexes and six-icosahedron complexes. In Mg_6Pd the six-icosahedron complex is substituted for a U_2F_9 unit of octahedra and trigonal prisms.

As an unsolved problem Westin (1972) reports that slightly different phases appear upon heat treatment at relatively low temperatures of Ru_7Mg_{44}. It is obvious, from the description of the structures discussed, with their common skeleton, that there is a variety of ordered ways of filling the cavities of this skeleton with the different units.

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References

Hyde, B. G., Bursill, L. A., O'Keeffe, M. & Andersson, S. (1972). *Nature (London) Phys. Sci.* **237**, 35–38.

Nyman, H. (1978). Unpublished results.

Nyman, H., Andersson, S., Hyde, B. G. & O'Keeffe, M. (1978). *J. Solid State Chem.* In the press.

Samson, S. (1972). *Acta Cryst.* B**28**, 936–945.

Samson, S. & Hansen, D. A. (1972). *Acta Cryst.* B**28**, 930–935.

Westin, L. (1972). Thesis, Stockholm.

Westin, L. & Edshammar, L.-E. (1971). *Acta Chem. Scand.* **25**, 1480–1481.

Westin, L. & Edshammar, L.-E. (1972*a*). *Chem. Scr.* **3**, 15–22.

Westin, L. & Edshammar, L.-E. (1972*b*). *Acta Chem. Scand.* **26**, 3619–3626.