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Tetragonal trimagnesium ruthenium trideuteride, Mg_3RuD_3, containing dinuclear $[Ru_2D_6]^{12-}$ complex anions

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Abstract

Trimagnesium ruthenium trihydride, Mg_3RuH_3, and its deuteride were synthesized by reaction of magnesium and ruthenium powders at 883 K and 9 bar hydrogen (deuterium) pressure and structurally characterized by X-ray and neutron powder diffraction; space group $P4_2/mnm$, $a = 7.2729(4)$ Å, $c = 6.9302(7)$ Å (deuteride, $T = 298$ K), $Z = 4$. The structure can be described in terms of $[Ru_2D_6]^{12-}$ dianions in which deuterium surrounds ruthenium in a distorted T-shaped configuration with bond distances Ru–D = 1.712(4) Å (2×) and 1.709(9) Å (1×) and bond angles D–Ru–D = 170.3(3)° and 94.7(2)°. The Ru–Ru distance is 3.310(4) Å.

1. Introduction

The magnesium–ruthenium–hydrogen system contains at least four ternary phases [1], of which two have been structurally characterized: cubic dimagnesium ruthenium hexahydride, Mg_2RuH_6 [2, 3], crystallizing with the K_2PtCl_6-type structure and containing octahedral $[RuH_6]^{4-}$ complex anions; and orthorhombic dimagnesium ruthenium tetrahydride, Mg_2RuH_4, which was described [4] in terms of $[RuH_4]^{4-}$ complex anions that derive from the octahedral $[RuH_6]^{4-}$ complex by removal of two *cis* hydrogen ligands.

In this paper we report on the synthesis and structural characterization of the third ternary phase known in this system, namely tetragonal trimagnesium ruthenium trihydride, Mg_3RuH_3. It is the first example of a ternary metal hydride that contains a transition element with three terminal hydrogen ligands and whose structure can be described in terms of dinuclear complex anions. (For a recent review on complex transition metal hydrides see ref. 5.)

2. Experimental details

2.1. *Synthesis*

Mg_3RuH_3 and its deuteride were synthesized by mixing the elemental metal powders (magnesium: CERAC 99.6% purity, 400 mesh; ruthenium:

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Johnson–Matthey 3N) in a 3:1 molar ratio, pressing them into pellets and sintering them at 883 K for 7 days under a hydrogen (deuterium) atmosphere (D_2, Air Liquide 99.8%) at 9 bar pressure. After reaction the pellets had disaggregated into a fine, dark grey powder which was stable in air. For the deuteride 3 g of the compound were obtained in one single batch.

2.2. *X-ray and neutron powder diffraction*

The X-ray diffraction experiments were carried out on a Guinier camera (Enraf–Nonius) and a Guinier diffractometer (Huber) using Cu $K\alpha_1$ radiation. The patterns confirmed the formation of the ternary metal hydride reported previously [1] and showed the presence of intermetallic Mg_3Ru_2]6] as the main impurity phase. The film data (internal standard: silicon, $a = 5.4308$ Å) were indexed on a tetragonal cell with TREOR [7]. The refined cell parameters (deuteride: $a = 7.2729(4)$ Å, $c = 6.9302(7)$ Å), likely space group ($P4_2/mnm$ [8]) and diffraction intensities were consistent with an $FeGa_3$-type metal atom arrangement [6]. A structure refinement of this model based on the diffractometer data using DBWS9006 [9] converged at $R_{wp} = 14.56\%$ and $R_B = 6.29\%$, with a goodness of fit $S = 1.62$.

The hydrogen positions were determined on the deuteride by collecting neutron data on the diffractometer DMC [10] at the reactor SAPHIR at PSI, Villigen (sample mass 3 g, cylindrical vanadium container of 8 mm inner diameter, $T = 298$ K, $\lambda = 1.7012$ Å, Ge(311) monochromator, 2Θ range

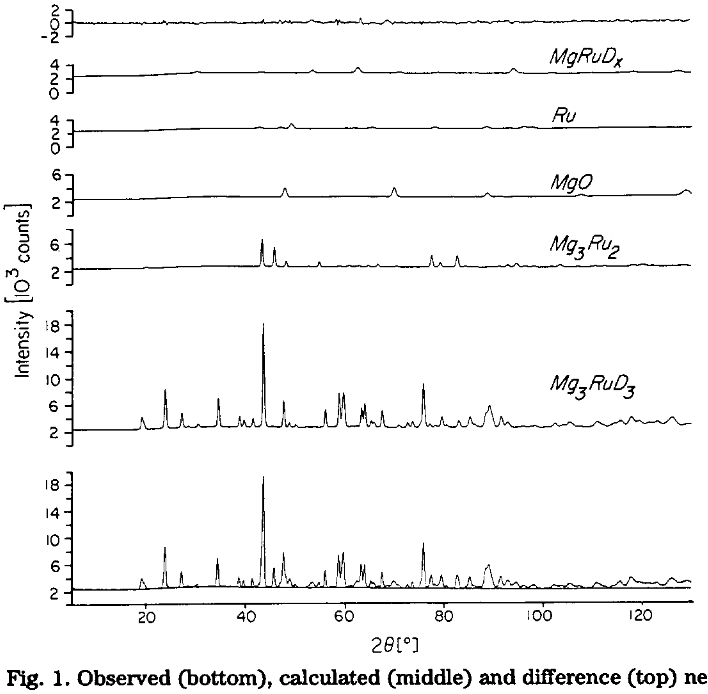


Fig. 1. Observed (bottom), calculated (middle) and difference (top) neutron diffraction patterns of Mg_3RuD_3, containing Mg_3Ru_2, MgO, ruthenium and $MgRuD_x$ impurity phases; $\lambda = 1.7012$ Å.

TABLE 1

Refinement results of Mg_3RuD_3 from neutron diffraction data (estimated standard deviations in parentheses)

Atom	Site	x	y	z	U_{iso} (10^{-2} Å^2)
Ru	4f	0.3391(4)	x	0	$\frac{1}{3}U_{iso}$(Mg1)
Mg1	4c	0	$\frac{1}{2}$	0	0.81(5)
Mg2	8j	0.1537(5)	x	0.2811(5)	U_{iso}(Mg1)
D1	8j	0.3531(5)	x	0.7538(6)	3.6(1)
D2[a]	8i	0.1362(13)	0.2205(8)	0	U_{iso}(D1)

Space group $P4_2/mnm$ (No. 136).
Cell parameters $a = 7.2729(4)$ Å, $c = 6.9302(7)$ Å.
Agreement indices $R_p = 2.68\%$, $R_{wp} = 3.54\%$, $S = 1.98$, $R_B = 5.68\%$.
[a] Population parameter 0.5.

3°–130°, step scan 0.1°, high resolution mode). The neutron-scattering lengths ($b_D = 0.6674 \times 10^{-12}$ cm, $b_{Mg} = 0.5375 \times 10^{-12}$ cm, $b_{Ru} = 0.721 \times 10^{-12}$ cm) were taken from ref. 11. The contributions of the following impurity phases were taken into account: Mg_3Ru_2 [6], MgO, ruthenium and cubic $MgRuD_x$ (perovskite derivative), not detected by X-rays (for neutron diffraction patterns see Fig. 1). Two symmetry-independent deuterium sites were found, D1 on position $8j$ and D2 on $8i$. The latter site was found to be a "split atom" position, having a population parameter of 0.5 and a site separation of [D2–D2] = 0.87 Å across a mirror plane. The refinement of this partially disordered structure model converged at $R_{wp} = 3.54\%$ and $R_B = 5.68\%$, with $S = 1.98$. No significant deviation from the stated stoichiometry could be found and the population parameters of the deuterium sites were fixed in the final stage of the refinement at 1.0 and 0.5 for D1 and D2 respectively. Attempts to refine the D2 position on the mirror plane (site $4f$) with full occupancy lead to a much poorer fit ($R_{wp} = 5.21\%$, $R_B = 11.12\%$, $S = 2.89$) and an unrealisticly high displacement parameter. The calculated pattern of an ordered model, with the same lattice metric, built in space group $P4_2/m$ (a subgroup of $P4_2/mnm$) contains significant additional peaks that were not observed in the experimental pattern at 298 K. The structural parameters are summarized in Table 1 and a list of interatomic distances and bond angles is given in Table 2.

3. Results and discussion

The basic structural unit of Mg_3RuD_3 is a distorted bicapped trigonal prism of magnesium atoms which is centred by ruthenium. The prisms are connected in pairs via uncapped rectangular faces and the pairs are connected via corners to a three-dimensional network. The capping magnesium atoms (Mg1) are surrounded by the corner atoms (Mg2) and form together a distorted b.c.c.-type configuration (Fig. 2).

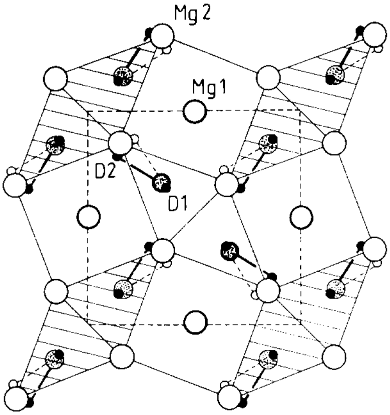
TABLE 2

Interatomic distances (Å) up to 3.4 Å and bond angles (deg) for Mg_3RuD_3. D2 site disordered with population parameter 0.5 (estimated standard deviations in parentheses)

Mg1	–D2	2.261(7)	D1	–Ru	1.712(4)
	–2 Ru	2.730(3)		–Mg2	2.065(5)
	–D2	3.094(9)		–2 Mg2	2.195(5)
	–4 Mg2	3.145(4)		–D2	2.516(7)
	–4 D1	3.263(4)		–D2	2.760(8)
	–4 D1	3.291(4)		–D1	3.022(5)
	–4 Mg2	3.375(4)		–D2	3.200(6)
				–2 Mg1	3.263(4)
Mg2	–D2	2.012(4)		–2 Mg1	3.291(4)
	–D1	2.065(5)			
	–2 D1	2.195(5)	D2	–D2	0.87(1)
	–Ru	2.726(4)		–Ru	1.709(9)
	–2 Ru	2.746(4)		–2 Mg2	2.012(4)
	–Mg2	3.034(5)		–Mg1	2.261(7)
	–2 Mg1	3.145(4)		–2 D1	2.516(7)
	–Mg2	3.162(5)		–2 D1	2.760(8)
	–2 Mg1	3.375(4)		–Mg1	3.094(9)
				–2 D1	3.200(6)
Ru	–D2	1.709(9)			
	–2 D1	1.712(4)			
	–2 Mg2	2.726(4)	D1–Ru–D1		170.3(3)°
	–2 Mg1	2.730(3)	D1–Ru–D2		94.7(2)°
	–4 Mg2	2.746(4)			
	–Ru	3.310(4)			

Ruthenium has three terminal deuterium ligands that form a slightly distorted T-shaped configuration with bond distances Ru–D1 = 1.712(4) Å (2×) and Ru–D2 = 1.709(9) Å (1×) and bond angles D1–Ru–D1 = 170.3(3)° and D1–Ru–D2 = 94.7(2)°. The two Ru–D1 bonds point towards the centres of the triangular prism faces, whereas the Ru–D2 bond points to the split atom position near the centre of the expanded prism edge, *i.e.* that opposite to the rectangular prism face joining the prisms in pairs (Fig. 3). The separation of the split atom sites (D2–D2 = 0.87 Å) suggests that the deuterium disorder is thermally activated.

A bonding description of Mg_3RuD_3 in terms of divalent magnesium cations and monomeric $[RuD_3]^{6-}$ anions implies an unusual 17-electron count for the anion complex. A more satisfactory description postulates the presence of dimeric $[Ru_2D_6]^{12-}$ complex anions in which the two ruthenium atoms share an electron pair across the common rectangular face of the trigonal prism pair as shown in Fig. 3. In this case Mg_3RuD_3 obeys the 18-electron rule, although the situation is quite unusual in view of the observed Ru–Ru distance of 3.31 Å, which is much longer than that usually found for Ru–Ru two-electron bonds in complexes such as binuclear carbonylate, $[Ru_2(CO)_8]^{2-}$, in which the Ru–Ru distance is 2.94 Å [12].



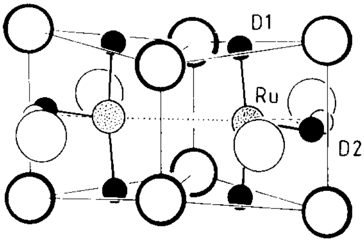


Fig. 2. Tetragonal structure of Mg_3RuD_3 projected along [001]: large circles, Mg atoms, medium circles filled by dots, Ru atoms; small circles, D atoms; dashed polyhedra, trigonal prisms around ruthenium at $z=\frac{1}{2}$, central polyhedron around ruthenium at $z=0$.

Fig. 3. Dimeric $[Ru_2D_6]^{12-}$ anion surrounded by a pair of bicapped magnesium prisms (point group symmetry *mmm*): prism corner atoms, Mg2 (thick open circles); prism capping atoms, Mg1 (thin open circles); thin lines, Mg–Mg contacts; thick lines, Ru–D bonds; dotted line, direction of hypothetical Ru–Ru bond.

Interestingly, a similar situation with unusually long Ru–Ru distances occurs in the recently reported ternary deuteride Mg_2RuD_4, whose structure was described [4] in terms of monomeric $[RuD_4]^{4-}$ complex anions having 16 electrons. The ruthenium atoms in this compound form zigzag chains with Ru–Ru distances of 3.24 Å. An alternative description in terms of polymeric $[RuD_4]_n^{4n-}$ anions in which each ruthenium atom shares electron pairs with its two ruthenium neighbours would be in accordance with the 18-electron rule. Clearly, theoretical calculations are necessary to confirm these hypotheses.

Acknowledgments

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