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Crystal growth, structure determination and magnetism of a new hexagonal rhodate: Ba₉Rh₈O₂₄

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Single crystals of Ba₉Rh₈O₂₄, grown from a molten potassium carbonate flux, crystallize in the spacegroup *R*3c with lattice parameters of *a* = 10.0899(4) and *c* = 41.462(2) Å. Magnetic measurements on oriented single crystals reveal the existence of magnetic anisotropy.

During recent years, there has been much interest in the preparation and investigation of oxides structurally related to the 2H hexagonal perovskites, the prototype of which, Sr₄PtO₆, was first prepared by Randall and Katz¹ and forms in the K₄CdCl₆ structure type. As shown by Darriet and Subramanian,² and more recently by Darriet and Perez-Mato,³ the structures of these oxides can all be described as resulting from stacking sequences of *m*[A₃O₉] layers and *n*[A₃A'O₆] layers, with the subsequent filling of the interstitial octahedral sites. The general formula that can be derived from the stacking of such layers is: A_{3n+3m}A'_nB_{3m+n}O_{9m+6n} (*n*, *m* = integers, A = alkaline earth; A', B = large assortment of metals including alkali, alkaline earth, transition, main group, and rare earth metals). The structures are characterized by one-dimensional chains of face-sharing trigonal prisms and octahedra along the *c*-axis of the hexagonal unit cell.

Sr₄PtO₆ is the *n* = 1, *m* = 0 member of this family and consists of chains of alternating face-sharing octahedra and trigonal prisms. While many *n* = 1, *m* = 0 members are known, for example Sr₃NaRhO₆,⁴ Ca₃Co₂O₆,^{5,6} and Ca₃CuIrO₆,⁷ far fewer oxides with higher integer values of *n* and *m* have been prepared and structurally characterized. In addition, until recently, most structure determinations were based on Rietveld refinements of polycrystalline powders and few single crystals of any members, and in particular very few members with higher integer values of *n* and *m*, have been grown and structurally characterized. A recent example of the latter type includes Ba₈CoRh₆O₂₁ corresponding to the *m* = 5, *n* = 3 member.⁸ Other examples include Ba₆Ni₅O₁₅,⁹ Sr₄Ru₂O₉,¹⁰ and the incommensurate phases of Ba_{1+x}(Cu_xRh_{1-x})O₃ (*x* = 0.1605 and 0.1695) whose average structure is that of the *n* = 3, *m* = 4 member with a repeat sequence of five octahedra and one trigonal prism.¹¹ In this communication we report the first structural characterization of the *m* = 2, *n* = 1 member Ba₉Rh₈O₂₄ and the investigation of its magnetic properties.

Single crystals of Ba₉Rh₈O₂₄ were grown from a molten potassium carbonate flux. BaCO₃ and Rh metal powder (6:1 molar ratio) were mixed with a 10 fold mass excess of K₂CO₃. The alumina crucible was heated in air to 1050 °C, held for 48 h, and then quickly cooled to room temperature. The crystals were isolated manually by dissolving the flux in water.

An approximate [110] view is shown in Fig. 1. The structure is characterized by infinite chains containing groups of seven face-sharing RhO₆ octahedra separated by one face-sharing RhO₆ trigonal prism. These chains are in turn separated from one another by chains of Ba cations. The metal–oxygen bond distances [Rh1–O1 2.020(6), Rh2–O2 2.008(6), Rh2–O1 2.035(6), Rh3–O3 2.003(7), Rh3–O2 2.035(6), Rh4–O4 1.969(10), Rh4–O3 2.048(7), Rh5–O4 2.012(12) Å] are typical

for oxides of this type. Intrachain Rh–Rh bond distances [Rh1–Rh2 2.523(1), Rh2–Rh3 2.455(1), Rh3–Rh4 2.637(2), Rh4–Rh5 2.750(1) Å] can be considered non-bonding.

Ba₉Rh₈O₂₄ represents the first structurally characterized *m* = 2, *n* = 1 member of this family, and more interestingly one of only a few single crystal compositions which are commensurate and not of the *n* = 1, *m* = 0 structure type. It is worth noting that this compound consists of the longest octahedra repeat sequence structurally characterized to date and structurally approaches the other end member of this family, *n* = 0, *m* = 1, the BaNiO₃ hexagonal perovskite structure. Compounds with chains consisting of 5 (Sr₆Rh₅O₁₅)¹² and 6 (Ba₈CoRh₆O₂₁) face-sharing octahedra separated by one face-sharing trigonal prism are known. In these and related oxides,⁶ large magnetic anisotropies have been observed as a function of crystal orientation. To investigate the magnetic behavior of Ba₉Rh₈O₂₄, susceptibility measurements were obtained using a large single crystal weighing 5.53(1) mg.[†]

The plot of susceptibility as a function of crystal orientation measured at 2 K is shown in Fig. 2. A beautiful regular sinusoidal variation in the susceptibility is clearly evident. The maxima in the susceptibility correspond to a parallel alignment of the hexagonal *c*-axis (*i.e.* the [Rh₈O₂₄]_∞ chain direction) with the applied field and the minima correspond to a 90 degree rotation from that position, or a perpendicular orientation of the *c*-axis relative to the magnetic field. Susceptibility measurements with the crystal oriented parallel and perpendicular with respect to the magnetic field are shown in Fig. 3, where the two curves diverge below *ca.* 100 K, indicating the onset of the

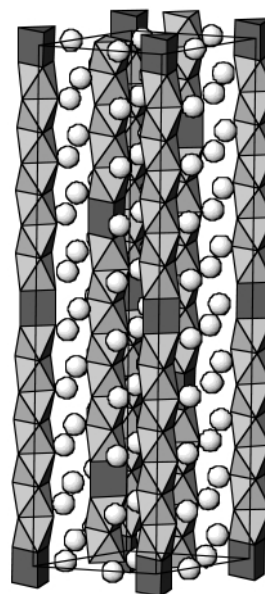


Fig. 1 Approximate [110] view of the structure of Ba₉Rh₈O₂₄. Dark grey: RhO₆ trigonal prisms; grey: RhO₆ octahedra; light grey: Ba atoms.

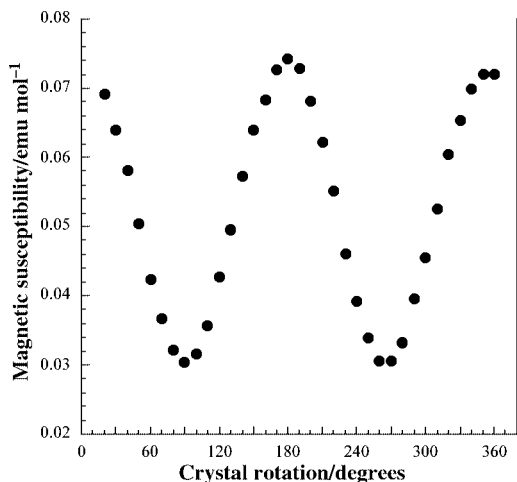


Fig. 2 Magnetic susceptibility of a single crystal of $\text{Ba}_9\text{Rh}_8\text{O}_{24}$ as a function of crystal orientation with respect to the applied magnetic field measured at 2 K and 5 kG. The maxima occur for the crystal's c -axis aligned parallel with the applied field.

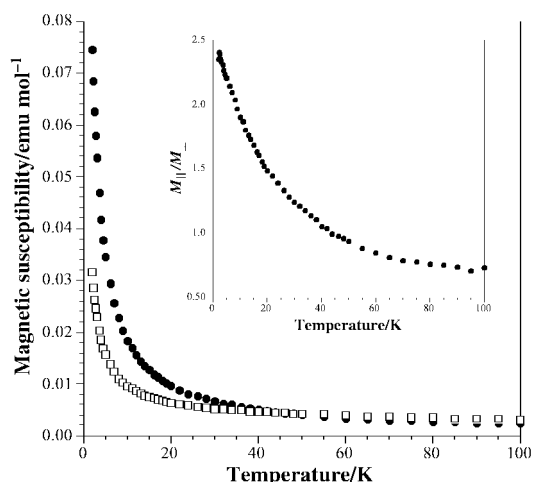


Fig. 3 Temperature dependence of the magnetic susceptibility of a single crystal of $\text{Ba}_9\text{Rh}_8\text{O}_{24}$ oriented parallel (●) and perpendicular (□) with respect to the applied field at 5 kG. Inset: temperature dependence of the magnetic anisotropy (defined as the ratio between the susceptibility of a single crystal oriented parallel and perpendicular with respect to the applied field).

magnetic anisotropy. The inset in Fig. 3 is a plot of the magnitude of the magnetic anisotropy, M_{\parallel}/M_{\perp} , as a function of temperature.†

The issue of oxidation states for the rhodium and their location in this chain structure is currently not possible to resolve. In order to charge balance $\text{Ba}_9\text{Rh}_8\text{O}_{24}$, oxidation states can be distributed as six Rh^{4+} and two Rh^{3+} . A bond valence analysis proved inconclusive, and so one might hope to gain insight into the oxidation states from the magnetic susceptibility data. Assuming low spin rhodium in octahedral coordination, the Rh^{4+} , d^5 , would each contribute one unpaired electron, while Rh^{3+} , d^6 , would contribute no unpaired electrons. Unfortunately, the magnetic data cannot be fit to Curie-type behavior, making it impossible to check the above assignment.

Finally, the presence of the non-magnetic Rh^{3+} in the chain, would break any exchange interactions between Rh^{4+} sites, leading to a disruption of magnetic interactions within the chain. This should result in the formation of small magnetic units along the chain. The anisotropy that is observed at low temperature can potentially be due to an anisotropy in the

exchange interaction between rhodium atoms in these small units or, alternatively, by irregular Rh^{4+} octahedra, resulting in different g -factors for g_{\parallel} and g_{\perp} . This is an area of further investigation and beyond the scope of this communication.

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Notes and references

† *Crystal data:* A black hexagonal prism was epoxied onto the end of a thin glass fiber. X-Ray intensity data were measured at 293 K using a Bruker SMART APEX CCD-based diffractometer system using Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). $\text{Ba}_9\text{Rh}_8\text{O}_{24}$, $M = 2443.34$ g mol $^{-1}$, rhombohedral, space group $R\bar{3}c$ (no. 167), $a = 10.0899(4)$, $c = 41.462(2)$ Å, $V = 3655.6(3)$ Å 3 , $Z = 6$, $D_c = 6.659$ Mg m $^{-3}$, $\mu(\text{Mo-}K\alpha) = 19.622$ mm $^{-1}$, crystal size: $0.24 \times 0.11 \times 0.10$ mm, θ range 2.38 – 33.16° , independent reflections 1551 ($R_{\text{int}} = 0.0312$), data/restraints/parameters 1551 / 0 / 66. Structure solved and refined using SHELXTL Version 5.1. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with the program SADABS (min., max. transmission = 0.1341, 0.2694). Final $R1$ (all data) = 0.0524, $wR2$ (all data) = 0.0992.

Atomic coordinates and equivalent isotropic displacement parameters:

Atom	x	y	z	$U_{\text{eq}}/\text{\AA}^2$
Ba(1)	0.3223(1)	0.9932(1)	0.0273(1)	0.012(1)
Ba(2)	0.3519(1)	0	1/4	0.010(1)
Rh(1)	0	0	0	0.006(1)
Rh(2)	0	0	0.9392(1)	0.008(1)
Rh(3)	0	0	0.8800(1)	0.006(1)
Rh(4)	0	0	0.8163(1)	0.011(1)
Rh(5)	0	0	3/4	0.014(1)
O(1)	0.1581(7)	0.1566(7)	0.0301(2)	0.010(1)
O(2)	0.8377(7)	0.9935(8)	0.9101(1)	0.008(1)
O(3)	0.8518(9)	0.8438(9)	0.8490(2)	0.022(2)
O(4)	0.8417(13)	0.9600(20)	0.7839(3)	0.080(6)

CCDC reference number 164826. See <http://www.rsc.org/suppdata/cc/b1/b104513j/> for crystallographic data in CIF or other electronic format.

‡ *Magnetism:* Magnetic measurements were collected on a single crystal of $\text{Ba}_9\text{Rh}_8\text{O}_{24}$ weighing 5.53(1) mg using a Quantum Design MPMS XL SQUID magnetometer. Aligned crystal measurements were performed using a Quantum Design Single Crystal Rotator attachment. The crystal was affixed to the rotator using standard vacuum grease. The crystal was rotated in 10° steps through 360° at 2 K with an applied field of 5 kG; knowing the initial orientation makes it possible to correlate the maxima and minima to the crystal alignment. Temperature dependence measurements were taken at a position corresponding to a maximum and a minimum in susceptibility at 5 kG. The moment of the sample holder was corrected for using the Automatic Background Subtraction software by Quantum Design.

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