Supporting Information
Complex Magnetic Order in Topochemically Reduced Rh(I)/Rh(III)
LaM_{0.5}Rh_{0.5}O_{2.25} (M = Co, Ni) phases.

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1. Structural Characterisation of LaCo$_{0.5}$Rh$_{0.5}$O$_3$.

![Image](image.png)

**Figure S1.** Observed, calculated and difference plots from the structural refinement of LaCo$_{0.5}$Rh$_{0.5}$O$_3$ against SXRD data collected at room temperature.

| Atom  | Site  | $x$     | $y$   | $z$     | Occupancy | Biso (Å$^2$) |
|-------|-------|---------|-------|---------|-----------|--------------|
| La    | 4$c$  | 04710(1) | 1/4   | 0.5055(2) | 1         | 0.65(1)    |
| Co/Rh | 4$b$  | 0       | 0     | 1/2     | 0.5/0.5   | 0.10(1)    |
| O(1)  | 4$c$  | 0.002(1) | 1/4   | 0.403(2) | 1         | 0.30(1)    |
| O(2)  | 8$d$  | 0.210(1) | 0.022(1) | 0.801(1) | 1         | 0.30(1)    |

LaCo$_{0.5}$Rh$_{0.5}$O$_3$ space group $Pnma$ (#62)

$a = 5.5722(1)$ Å, $b = 7.8837(3)$ Å, $c = 5.5860(2)$ Å, volume = 245.39(1) Å$^3$

Formula weight = 267.83 g mol$^{-1}$, $Z = 2$

Radiation source: Synchrotron X-ray, $\lambda = 0.8268$ Å

Temperature: 298 K

$R_p = 2.71\%$, $wR_p = 4.04\%$, $R_{Bragg} = 1.31\%$

**Table S1.** Parameters from the structural refinement of LaCo$_{0.5}$Rh$_{0.5}$O$_3$ against SXRD data collected at room temperature.
2. Structural Characterisation of LaNi$_{0.5}$Rh$_{0.5}$O$_3$.

![Figure S2. Observed, calculated and difference plots from the structural refinement of LaNi$_{0.5}$Rh$_{0.5}$O$_3$ against SXRD data collected at room temperature.](image)

| Atom | Site | x     | y     | z     | Occupancy | Biso (Å$^2$) |
|------|------|-------|-------|-------|-----------|--------------|
| La   | 4c   | 04635(1) | ¼     | 0.5009(9) | 1         | 0.65(1)     |
| Ni/Rh | 4b   | 0      | 0     | ½     | 0.5/0.5   | 0.10(1)     |
| O(1) | 4c   | 0.023(1) | ¼     | 0.385(2) | 1         | 0.30(1)     |
| O(2) | 8d   | 0.224(1) | 0.041(1) | 0.783(1) | 1         | 0.30(1)     |

LaNi$_{0.5}$Rh$_{0.5}$O$_3$ space group *Pnma* (#62)

\[ a = 5.5531(1) \text{ Å}, \ b = 7.8452(3) \text{ Å}, \ c = 5.5640(1) \text{ Å}, \ \text{volume} = 242.40(1) \text{ Å}^3 \]

Formula weight = 267.71 g mol$^{-1}$, Z = 2

Radiation source: Synchrotron X-ray, \( \lambda = 0.8268 \) Å

Temperature: 298 K

\( R_p = 2.29 \% \), \( wR_p = 3.61 \% \), \( R_{Bragg} = 1.03 \% \)

**Table S2.** Parameters from the structural refinement of LaNi$_{0.5}$Rh$_{0.5}$O$_2$ against SXRD data collected at room temperature.
3. Thermogravimetric Characterisation of LaCo$_{0.5}$Rh$_{0.5}$O$_{3-x}$.

Figure S3. Thermogravimetric data collected while heating LaCo$_{0.5}$Rh$_{0.5}$O$_{3-x}$ under a 10:90 H$_2$:N$_2$ gas flow. X-ray powder diffraction data indicates the sample decomposed to a mixture of La$_2$O$_3$, Co and Rh, losing 4.74% mass. This indicates an initial composition of LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25(1)}$. 
4. Thermogravimetric Characterisation of LaNi$_{0.5}$Rh$_{0.5}$O$_{3-x}$.

**Figure S4.** Thermogravimetric data collected while heating LaNi$_{0.5}$Rh$_{0.5}$O$_{3-x}$ under a 10:90 H$_2$:N$_2$ gas flow. X-ray powder diffraction data indicates the sample decomposed to a mixture of La$_2$O$_3$, Ni and Rh, losing 5.11% mass. This indicates an initial composition of LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25(1)}$ when the 9.2 weight % LaNi$_{0.5}$Rh$_{0.5}$O$_3$ observed in NPD data is taken into account.
5. Structural Characterisation of LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$ and LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25}$ at 298K.

| Atom     | Site | x    | y    | z    | Occupancy | B$_{iso}$ (Å$^2$) |
|----------|------|------|------|------|-----------|-------------------|
| La       | 4$b$ | $\frac{1}{2}$ | 0    | $\frac{1}{4}$ | 1         | 0.32(1)          |
| Co/Rh    | 4$c$ | 0    | 0    | 0    | 0.5/0.5 | 0.43(1)          |
| O (1)    | 8$h$ | 0.2139(2) | 0.2860(2) | 0    | 1         | 0.83(2)          |
| O (2)    | 4$a$ | 0    | 0    | $\frac{1}{4}$ | 0.25(1) | 0.83(2)          |

LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25(1)}$ - space group $I4/mcm$ (#140)

- $a = 5.6492(2)$ Å, $c = 7.3374(7)$ Å,
- Volume = 234.16(3) Å$^3$
- Formula weight: 255.83 g mol$^{-1}$, $Z = 4$
- Radiation source: Neutron, $\lambda = 1.594$ Å
- Temperature: 298 K
- $wR_p = 2.77\%$, $R_p = 2.18\%$, $R_{Bragg}$ 1.01%

Table S3. Parameters from the structural refinement of LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$ against NPD data collected at room temperature.

| Atom     | Site | x    | y    | z    | Occupancy | B$_{iso}$ (Å$^2$) |
|----------|------|------|------|------|-----------|-------------------|
| La       | 4$b$ | $\frac{1}{2}$ | 0    | $\frac{1}{4}$ | 1         | 0.43(1)          |
| Ni/Rh    | 4$c$ | 0    | 0    | 0    | 0.5/0.5 | 0.52(1)          |
| O (1)    | 8$h$ | 0.215(2) | 0.284(2) | 0    | 1         | 0.91(2)          |
| O (2)    | 4$a$ | 0    | 0    | $\frac{1}{4}$ | 0.24(2) | 0.91(2)          |

LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25(1)}$ - space group $I4/mcm$ (#140)

- $a = 5.6407(1)$ Å, $c = 7.1794(7)$ Å,
- Volume = 228.44(2) Å$^3$
- Formula weight: 255.71 g mol$^{-1}$, $Z = 4$
- 90.2(3) weight percent
- $R_{Bragg}$ 1.03%

Table S4. Parameters from the structural refinement of LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25}$ against NPD data collected at room temperature.

| Cation | Anion | Bond length (Å) | Bond angle (°) |
|--------|-------|-----------------|----------------|
| M/Rh   | O(1) $\times$ 4 | 2.018(1) | 163.59(3) ° |
| M/Rh   | O(2) $\times$ (2 $\times$ $\frac{1}{4}$) | 1.834(1) | 164.2(3) ° |
| La     | O(1) $\times$ 4 | 2.930(1) | 163.59(3) ° |
| La     | O(1) $\times$ 4 | 2.507(1) | 164.2(3) ° |
| La     | O(2) $\times$ (4 $\times$ $\frac{1}{4}$) | 2.825(1) | 163.59(3) ° |

Table S5. Selected bond lengths and angles from the refined structures of LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$ and LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25}$. 

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6. HAXPES.

**Figure S5.** HAXPES data from LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$, including (a) survey spectrum, (b) Rh 3$p$ / O 1$s$ core level spectra, and (c) valence band spectrum. In (c) the position of the Fermi level $E_F$ at 0 eV is indicated.
7. Magnetic measurements in the presence of elemental Ni and Co impurities via the ‘ferrosubtraction’ method.

Procedure used to measure the magnetization of samples containing elemental nickel: The magnetization of elemental Ni and Co is observed to saturate in applied magnetic fields of more than 2 T. Thus the paramagnetic susceptibility of a bulk sample can be measured in the presence of elemental Ni and Co impurities by measuring the gradient of magnetization-field isotherms in applied fields larger than 2 T. As shown in Figure S6.

To this end the magnetization of samples was measured in a series of 5 fields between 3 T and 5 T. The magnetization vs. field data were fitted to a linear function, the gradient of which is the paramagnetic susceptibility of the bulk sample and the intercept is the saturated ferromagnetic moment of the sample. Data points with large errors were excluded from fits. All fits had at least 4 data points. This procedure was repeated at 5 K intervals between 5 K and 300 K to measure the temperature dependent susceptibility of samples.

![Graph](image)

**Figure S6.** Magnetisation of LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25}$ measured as a function of applied field at 300 K. A linear fit to high-field region (H > 25000 Oe) yields a gradient which is the paramagnetic susceptibility of the sample, and an intercept which is the saturated ferromagnetic moment of the sample.
8. Structural Characterisation of LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25}$ at 2K.

**Figure S7.** Observed calculated and difference plots from the structural refinement of LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25}$ against NPD data collected at 2 K using the D1B instrument. Black and red and blue tick marks indicated peak positions for the majority phase, a LaNi$_{0.5}$Rh$_{0.5}$O$_{3}$ secondary phase and contributions from the vanadium sample holder, respectively.
| Atom     | Site | x     | y     | z     | Occupancy | $B_{iso}$ (Å²) |
|----------|------|-------|-------|-------|-----------|----------------|
| La       | 4b   | ½     | 0     | ¼     | 1         | 0.38(1)       |
| Ni/Rh    | 4c   | 0     | 0     | 0     | 0.5/0.5  | 0.51(2)       |
| O (1)    | 8h   | 0.217(3) | 0.282(3) | 0 | 1         | 0.86(2)       |
| O (2)    | 4a   | 0     | 0     | ¼     | 0.24(1)  | 0.86(2)       |

LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25(1)}$ - space group $I4/mcm$ (#140)
- $a = 5.638(1)$ Å, $c = 7.178(1)$ Å,
- Volume = 228.16(2) Å³,
- Formula weight: 255.71 g mol$^{-1}$, Z = 4,
- 85.2(3) weight percent
- $R_{Bragg}$ 1.03%

LaNi$_{0.5}$Rh$_{0.5}$O$_3$ - space group $Pnma$ (#62)
- $a = 5.507(8)$ Å, $b = 7.798(7)$ $c = 5.534(4)$ Å,
- Volume = 237.6(4) Å³,
- Formula weight: 267.71 g mol$^{-1}$, Z = 4,
- 14.8(3) weight percent

Radiation source: Neutron, $\lambda = 2.52$ Å
Temperature: 2 K
$wRp = 2.36\%$; $Rp = 1.76\%$

**Table S6.** Parameters from the structural refinement of LaNi$_{0.5}$Rh$_{0.5}$O$_{2.25}$ against NPD data collected at 2 K.
9. Magnetic Characterisation of LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$.

Figure S8. Magnetisation data collected as a function of temperature using the ferrosubtraction technique from LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$. Top panel shows fit of paramagnetic susceptibility to the Curie-Weiss Law in the range 210 < T/K < 300. Middle panel shows paramagnetic susceptibility. Bottom panel shows saturated Ferromagnetic moment.
Figure S9. Magnetisation-field data collected from LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$ after cooling in an applied field of 50,000 Oe.
| Atom   | Site | x   | y   | z   | Occupancy | $B_{iso}$ (Å²) |
|--------|------|-----|-----|-----|-----------|----------------|
| La     | 4b   | ½   | 0   | ¼   | 1         | 0.22(1)       |
| Co/Rh | 4c   | 0   | 0   | 0   | 0.5/0.5   | 0.41(1)       |
| O (1)  | 8h   | 0.2139(2) | 0.2860(2) | 0   | 1         | 0.63(2)       |
| O (2)  | 4a   | 0   | 0   | ¼   | 0.25(1)   | 0.63(2)       |

LaCo$_0.5$Rh$_{0.5}$O$_{2.25}$ - space group $I4/mcm$ (140)

$a = 5.626(1)$ Å, $c = 7.309(1)$ Å,

Volume = 231.3(1) Å$^3$

Formula weight: 255.83 g mol$^{-1}$, $Z = 4$

| Atom   | x   | y   | z   | $m_x/\mu_B$ | $m_y/\mu_B$ | $m_z/\mu_B$ |
|--------|-----|-----|-----|-------------|-------------|-------------|
| Co(1)  | 0   | 0   | 0   | 1.30(11)    | 0           | 1.19(6)     |
| Co(2)  | ½   | ½   | 0   | -1.30(11)   | 0           | -1.19(6)    |
| Co(3)  | 0   | 0   | ½   | 1.30(11)    | 0           | -1.19(6)    |
| Co(4)  | ½   | ½   | ½   | -1.30(11)   | 0           | 1.19(6)     |

Radiation source: Neutron, $\lambda = 2.52$ Å

Temperature: 2 K

$wR_p = 2.17\%$, $R_p = 1.61\%$, $R_{Bragg}$ 1.03%  

**Table S7.** Nuclear and magnetic structure of LaCo$_{0.5}$Rh$_{0.5}$O$_{2.25}$ determined by refinement against NPD data collected at 2K. The magnetic model is a combination of an $mM_5^+$ irreducible representation describing the $m_x$ component of the ordered moments (magnetic space group 60.432) and an $m\Gamma_1^+$ irreducible representation describing the $m_z$ combination of the ordered moments (magnetic space group 140.541). The cobalt centres in the magnetic model have an occupancy of 0.5.