We present the synthesis and structural characterisation of a transition metal oxide hydride, LaSrCoO$_2$H$_{0.7}$, which adopts an unprecedented structure in which oxide chains are bridged by hydride anions to form a two-dimensional extended network. The metal centers are strongly coupled by their bonding with both oxide and hydride ligands to produce magnetic ordering up to at least 350 K. The synthetic route is sufficiently general to allow the prediction of a new class of transition metal-containing electronic and magnetic materials.
gan to increase and probably reflects the approach of the phase transition. (Fig. 1B). These results do not allow us to determine precisely the Néel temperature, but show that it is likely to be above 350 K. The muon site is likely to be similar to that found in Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$, in which the muon is believed to form an O–$\mu^+$ bond with a bond length of $\sim$1 Å (9, 10) However the measured muon precession frequency for these materials is much lower, corresponding to 2.32 and 3.5 mT for Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$ respectively (10). Such low internal fields are associated with magnetic moments less than 0.1 $\mu_B$.

The precession frequency in the present case is $>200$ times greater than in Sr$_2$CuO$_3$, which is consistent with the moment refined from powder neutron diffraction on 1. The Néel temperatures of Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$ are $\sim$ 5 K and $\sim$ 11 K respectively. The much larger value of $T_N$ observed for 1 points to a large interchain coupling, which is surprising because the lattice constants in the interchain direction are larger than in Sr$_2$CuO$_3$ and Ca$_2$CuO$_3$.

After the verification of long-range magnetic order at room temperature by $\mu$SR, a simple antiferromagnetic (AF) ordering model, with antiparallel spin alignment of all neighboring Co spins, was incorporated in refinement of the neutron data. Although this addition gave a satisfactory fit to the magnetic reflections, the fit to the nuclear reflections was unsatisfactory ($\chi^2 = 5.15$, weighted profile residual ($R_{wp}$) = 5.55%) (7). A difference Fourier map was computed and revealed a strong peak of negative scattering density at (0, 1/2, 0) midway between the Co atoms along the b-axis at the vacant oxide anion position in the CoO$_2$–x sheets (7). Hydrogen is one of the few elements to have a negative neutron scattering length,(11) and therefore hydrogen was inserted into the model at this position. The refinement immediately converged at $\chi^2 = 1.96$, $R_{wp} = 3.43\%$ as shown in Fig. 2, demonstrating that 1 is the first extended transition metal oxide hydride.

The structural analysis was completed by a three histogram refinement of 2.4 Å and 1.59 Å neutron histograms together with the synchrotron data (Fig. 2). The quality of the fits demonstrates the correctness of the structural model, which gives a refined composition of LaSrCoO$_3$H$_{0.70(2)}$. The presence of a small amount of La$_2$O$_3$ is inconsistent with this composition (7). The ordered magnetic moment carried by the cobalt cations increases from 1.77(5)$\mu_B$ at 290 K to 1.95(4)$\mu_B$ at 2 K. The +1.7 oxidation state of Co deduced from the refined composition with a charge distribution assigning the $\sim$1 oxidation state to H is consistent with the position of the Co K-edge in LaSrCoO$_3$H$_{0.70(2)}$ (7) and the presence of hydride was confirmed chemically by quantitative mass spectrometric monitoring of the H$_2$O evolved simultaneously with oxidation of 1 under flowing O$_2$ at 272(5)$^\circ$C, which indicates 0.4 H$^-$ per formula unit; while necessarily less accurate than the structure refinement, this chemically confirms the presence of hydrogen. Chemical analysis (5) reveals 0.27% H by mass compared with 0.21% expected for LaSrCoO$_3$H$_{0.70(2)}$.

The structure (Fig. 3) consists of chains of CoO$_4$ squares sharing corners along a to form chains which are linked into a 2D array in the ab plane by H$^-$ bridges along b. The CoO$_2$ sheets in the ab plane of the starting material have been replaced with CoOH$_{0.7}$ sheets in the oxide hydride product, consistent with a reduction-insertion mechanism in which oxide vacancies are created in the xy plane followed by their filling by the H$^-$ anions. The Co(II) cations have a mean coordination number of 5.40(4), with the H$^-$ anions occupying the axial positions between the square plane of oxide anions. The Co–H distance of 1.80174(2) Å is shorter than either of the Co–O distances and this, coupled with the strong covalency expected for the interaction between Co$^{2+}$ and H$^-$, produces strong AF coupling between the Co(II) cations within the 2D sheets. The effect of the hydride anions on bridging the Sr$_2$CuO$_3$-like 1D chains is qualitatively demonstrated by comparing $T_N$ of above 300 K here with 11 K in Sr$_2$CuO$_3$ itself. A qualitative comparison between H$^-$ and O$^{2-}$ oxide bridges can be made by noting that LaSrCoO$_3$H$_{0.70}$ (6) has a Néel temperature of 110 K, with a similar concentration of bridging anions in the ab plane.

The high AF ordering temperature of LaSrCoO$_3$H$_{0.70}$ demonstrates that the H$^-$ anion can strongly couple transition metal cations electronically. To confirm this supposition, we have performed spin wave calculations to crudely model the effect of coupling the CoO$_3$ oxide chains by H$^-$ anions. We find that increasing the effective exchange between chains in one direction to close to the intrachain exchange $J$ is sufficient to raise the Néel temperature to the order of $J/k_B$ (where $J$ is the intrachain exchange), even if the coupling in the orthogonal interchain direction is quite weak; the size of the moment will then be near the full value (this scenario is appropriate for LaSrCoO$_3$H$_{0.70}$, in which we observe a large moment and $T_N \sim 350$ K which is of the order of $J/k_B$).

If, however the interchain exchange is weak in both directions, the Néel temperature is largely controlled by that weak interchain exchange and the size of the moment is greatly reduced because of quantum fluctuations (this scenario is appropriate for Sr$_2$CuO$_3$, in which the moment is reduced to 0.06$\mu_B$ and $T_N = 11$ K (8)). This stark difference in magnetic properties highlights the crucial role played by the bridging H$^-$ ions, and confirms that they are capable of coupling transition metal centres equally as effectively as O$^{2-}$ anions.

The H$^-$ anions are exclusively located in the transition metal containing layers in the structure, in contrast to oxohalides such as Sr$_2$CoO$_3$Cl(3) in which the halide anions occupy the apical positions within the electronically inactive rock salt layers. The demonstration that transition metal oxide hydrides can be isolated now suggests such species should be considered when discussing chemical and catalytic processes involving transition metal oxides, such as the spillover process(12) where only H$^-$ and OH$^-$ have been invoked.(13) The site-specific insertion of the H$^-$ anions into the ox-
ide sheets may reflect the enhanced bridging interaction with the transition metal cations in this site, or be due to a topotactic transformation mechanism in which anion vacancies present in an LaSrCoO$_{3.5}$ intermediate are filled with hydride anions. The combination of cation reduction with anion insertion is unusual for a topotactic solid-state transformation, but may prove to be a general route to transition metal oxide hydrides, opening up previously uncharted areas in electronic and magnetic materials synthesis. Quantitative estimates of the strength of the exchange interaction demonstrate that the H$^-$ bridge couples metal centres as effectively as O$^{2-}$, although the different frontier orbital symmetry ($\sigma$ only in H$^-$, $\sigma + \pi$ in O$^{2-}$) promises interesting property differences to be revealed in future detailed studies of this new class of extended solid. (14)

References and notes
7. Full synthetic and structural characterization details are provided as supplemental data at Science online.
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Figure 1: (A) Muon spin rotation data from 1: The oscillations in the asymmetry demonstrate long-range magnetic order at all temperatures measured (up to 310 K) temperature dependence of (B) the relaxation rate of the oscillations (dotted line is a guide to the eye) and (C) the muon-spin rotation frequency and the corresponding magnetic field at the muon site. In (C) the line represents a fit to a phenomenological expression for the temperature dependence of the order parameter in a magnetic material. Good fits could be obtained by fixing the transition temperature at values in the range 350 to 450 K, demonstrating that the magnetic ordering temperature of 1 probably lies above 350 K.
Figure 2: Structural characterisation of $\text{LaSrCoO}_3H_{0.70}$ by simultaneous Rietveld refinement of (A) neutron diffraction and (B) synchrotron XRD data collected as described in (5), where full refinement details are also available. $\text{LaSrCoO}_3H_{0.70}$ adopts space group $\text{Immm}$, $a = 3.87093(4)\,\text{Å}$, $b = 3.60341(3)\,\text{Å}$, $c = 13.01507(10)\,\text{Å}$, $V = 181.541(3)\,\text{Å}^3$, La (50 % occupancy)/Sr (50 % occupancy) on 4i 0,0,0.35703(3), Co on 2a 0,0,0, O(1) on 4i 0,0,0.1673(2), O(2) on 2b 1/2, 0, 0, H on 2d 0, 1/2,0 70(2) % occupancy.
Figure 3: (A) The crystal structure of 1, LaSrCoO$_4$H$_{0.70}$ and its topotactic relation with (B) the LaSrCoO$_4$ starting material. 1 can be generated from LaSrCoO$_4$ by substitution of half of the equatorial O$^{2-}$ anions (circled in yellow) by H$^-$. Hydride ions and Sr/La cations are represented as yellow spheres and green spheres respectively and the oxide ion arrangements around the Co cations are illustrated by squares and octahedra in (A) and (B) respectively. Co–O(1) 2.1779(22) Å $\times$ 2, Co–O(2) 1.93549(2) Å $\times$ 2, Co–H 1.80174(2) Å $\times$ 2, Sr/La–O(1) 2.469(2) Å, 2.6633(3) Å $\times$ 4, Sr/La–O(2) 2.5902(3) Å $\times$ 2, Sr/La–H 2.6849(3) Å $\times$ 2 The bond angles within the CoO$_4$H$_{1.4}$ unit are all constrained to 90° or 180° by the symmetry of 1. (C) The coordination environments of the La/Sr (black sphere) and Co (blue sphere) sites in 1. Oxide and hydride anions are represented as red and yellow spheres, respectively. (D) The magnetic structure of 1 at room temperature. For increased clarity, only the Co cations are shown. The arrows represent the direction of the ordered magnetic moments.