Structure-property relationships and the mechanisms of multistep transitions in spin crossover materials and frameworks

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Abstract: Spin crossover frameworks and molecular crystals display fascinating collective behaviours. This includes multiple step transitions with hysteresis and a wide variety of long-range ordered patterns of high-spin and low-spin metal centres. From both practical and fundamental perspectives it is important to understand the mechanisms behind these collective behaviours. We study a simple model of elastic interactions and identify thirty-six different spin-state ordered phases. We observe spin-state transitions with between one and eight steps. These include both sharp transitions and crossovers, leading to both complete and incomplete spin crossover. We demonstrate structure-property relationships that explain these differences. These arise because through-bond interactions favour metal centres with different spin-states; whereas, through-space interactions typically favour the same spin-states. In general, rigid materials with longer range elastic interactions lead to transitions with more steps and more diverse spin-state ordering, which may explain why both are prominent in framework materials.

Introduction

Spin crossover (SCO) materials typically consist of a transition metal ion with a partially occupied d-shell, between \( d^4 \) and \( d^7 \), surrounded by several ligands. Depending on the physical environment (temperature, pressure, magnetic field, exposure to light, etc.) these materials can exist in either high spin (HS) or low spin (LS) states. In the solid state, long-range elastic interactions between metal centres couple to the local structural distortions caused by individual metal centres changing their spin-state. This causes a wide range of different thermodynamic behaviours, including first-order transitions with hysteresis, incomplete transitions, crossovers, and up to eight-step transitions.

Many different long-range ordered patterns of HS and LS metal centres, collectively known as antiferroelastic phases (Fig. 1), have been observed. This leads one ask what mechanism is responsible for these collective effects? and can one predict what other behaviours might exist? Beyond the fundamental interest in these questions, SCO materials and frameworks have been sought after for their many potential applications including high-density reversible memory, actuators, ultrafast nanoscale switches, thermometers, barometers and displays. Understanding the mechanisms that control the collective behaviours of SCO materials could significantly enhance their potential to be engineered for specific applications.

Recently, it has been suggested that frustrated elastic interactions are crucial for understanding multi-step transitions and antiferroelastic order in SCO materials. Frustration occurs whenever a system is unable to simultaneously minimize the energy of two or more competing interactions. For example, a mismatch between the equilibrium bond lengths of nearest and next nearest-neighbour bonds, has been shown to induce two-step transitions on the square lattice. However, the question of what mechanism is responsible for three- and four-step transitions, and the diversity of antiferroelastic orders reported remains open. In particular, the link between antiferroelastic order and the topology of the lattice remains largely unexplored.

Multi-step transitions have been reported for a variety of different molecular materials and frameworks on square arrays including Hofmann-type molecular frameworks, other coordination polymers and...
molecular crystals held together by supramolecular interactions. Hofmann-type frameworks that contain one metal species, M, that is SCO active and another, M’, that is diamagnetic have proved a particularly interesting playground for antiferroelasticity. We will discuss two families of Hofmann-type frameworks with the general formulae \([M(L)_nM'(L')_4]\) and \([M(L)_nM'(L')_2]\), where \(L\) is the ligand within the plane, \(L'\) is the ligand connecting layers, and \(n\) = 1 or 2 for bridging and monodentate ligands respectively. Henceforth we will refer to these as the 1n14 and 1n24 families respectively. Prototypical examples are \([Fe(pz)Pt(CN)_4]\) and \([Fe(pz)Au(CN)_2]_2\). These crystals have importantly different topologies, Figs. 2a,b. Nevertheless, in both families the SCO active \(M\) sites form simple square sublattices.

Antiferroelasticity has been observed in a number of other coordination polymers where the metal centres form two-dimensional \(M\) \(\rightarrow\) \(M'\) families of Hofmann frameworks, \(c\) the 1n02, \([M(L)_n(L')_2]\), family of coordination polymers, and \(d\) a simple square supramolecular crystal. In each case the elastic interactions, \(k_n\), between \(n\)th nearest neighbour SCO active \(M\) sites (grey circles) are marked. Non-SCO-active ions (\(M'\), black circles) and in-plane ligands (\(L'\), black lines) are also shown. All four classes of materials are described by the same model (Eq. 3), but with very different magnitudes and signs of the \(k_n\) due to the topological differences shown here.

In the 1n14 family (Fig. 2a) there are covalent bonds connecting the second and fifth nearest neighbour \(M\) sites but only weak through-space interactions connecting nearest, third and fourth neighbours. Whereas, for the 1n24 and 1n02 families (Fig. 2b) there are covalent bonds connecting the nearest and third nearest neighbour \(M\) sites and through-space interactions connecting the second, forth and fifth nearest neighbours. We will show below that through-bond interactions favour neighbouring metal centres with different spin-states (one high spin and the other low spin); whereas through-space interactions favour neighbouring metal centres with the same spin-states (both high spin or both low spin). This leads to important predicted structure-property relationship for SCO frameworks. We confirm these predictions via a detailed comparison with the experimental literature.

**Model**

We consider an arbitrary interaction, \(V_{ij}(r)\), between two SCO active \(M\) sites, \(i\) and \(j\). In a crystal the equilibrium structure minimises the total free energy, which includes the sum of \(V_{ij}(r)\) over all pairs \(i, j\). Thus, if the interactions are frustrated there is no guarantee that that any particular \(V_{ij}(r)\) is minimised in the equilibrium structure. The equilibrium separation between nearest neighbour metal centres in the HS phase, \(r_H\), is found experimentally to be larger than that in the LS phase, \(r_L\). We linearly interpolate between these two lengths:

\[
r_0 = \frac{r_H + r_L}{2}
\]

(1)

where \(\sigma_i = +1 (-1)\) when the \(i\)th \(M\) site is HS (resp. LS), \(R = (r_H + r_L)/2\) and \(\delta = (r_H - r_L)/4\).

We show in the supplementary information that, quadratically interpolating between \(V_{ij}(r_H)\), \(V_{ij}(\bar{R})\) and \(V_{ij}(r_L)\), allows us to write the Hamiltonian as

\[
\mathcal{H} = \frac{\Delta G}{2} \sum_{i,j} \sum_{n=1}^m \frac{k_n}{\bar{R}_n} \left\{ \frac{r_{i,j} - \eta_n [R + \delta (\sigma_i + \sigma_j)]}{2} \right\}^2
\]

(2)

where \(\Delta H\), \(\Delta S\) and \(\Delta G = \Delta H - T\Delta S\) are respectively the enthalpy, entropy and free energy differences between a single ion in the HS and LS states, \(k_n\) are the effective spring constants between the enthalpy, entropy and free energy differences between the HS and LS phases, \(\eta_n = 1, \sqrt{2}, 2, \sqrt{5}, 2\sqrt{2}, \ldots\) is the ratio of distances between the \(n\)th and 1st nearest-neighbour distances on the undistorted square lattice. \(\Delta S\) arises primarily from the softening of vibrational modes in the HS state, with smaller contributions from the changes in the spin and orbital degeneracies. Therefore, in all the calculations presented here we set \(\Delta S = 4k_B \ln 5\) (see Supplementary Information).

We solve this model in the ‘symmetric breathing mode approximation,’ i.e., we assume that for all nearest neighbours, \(r_{i,j} = x\), and that the topology of the lattice is not altered by the changes in the spin-states. This yields an effective Ising-Husimi-Temperley model in a longitudinal field

\[
\mathcal{H} \approx \sum_{n=1}^m J_n \sum_{\langle i,j \rangle_n} \sigma_i \sigma_j - \frac{J_{\infty}}{N} \sum_{i,j} \sigma_i \sigma_j + \frac{\Delta G}{2} \sum_i \sigma_i
\]

(3)
where, $J_n = k_n \eta_0^2 \delta^2$ is the effective interaction between the $n$th nearest-neighbour metal centres, $J_\infty = \delta^2 \sum_{n=1}^{\infty} (k_n \eta_0^2)$ is the long-range strain, $z_n$ is the coordination number for $n$th nearest neighbours and $N$ is the number of $M$ sites. The long-range strain has equal strength between all metal centres, distributing the impact of local molecular volume changes due to spin-state transitions over the lattice. Minimization over the instantaneous bond distance requires that $\left( \partial^2 \mathcal{H} / \partial x^2 \right) _{x=\eta} = 2J_\infty > 0$. Thus the crystal is dynamically unstable for $J_\infty < 0$, and we do not study parameters in that regime below.

For nearby metal centres joined via (networks of) covalent bonds one expects the metal-metal separation to be close to the minimum of the potential. Hence, one expects that the spring constant, $k_n$, is large and positive (i.e., an antiferroelastic interaction). For through-space interactions a separation larger than the minimum of the potential leads to a negative (ferroelastic) spring constant, $k_n \approx \partial^2 V_{ij} / \partial r^2 |_{r=\eta}$ (see Supplementary Information), as illustrated in Fig. 3.

As through-space interactions can be antiferroelastic or ferroelastic, one might find that both $k_1 > 0$ and $k_2 > 0$ for some materials in any family of coordination polymers and supramolecular crystals. We will see below that in this case the long-range strain dominates and the SCO transition is always one step. The three families of frameworks that we consider embody two distinct topologies with the framework of our model, Fig. 2. In the 1n14 family $k_2$ and $k_3$ are through-bond whereas $k_1$, $k_3$ and $k_4$ are through-space. Therefore, one expects $k_2 < k_3 > k_1$, but it is reasonable to expect that in many materials $k_1 < k_3 < k_2 < 0$. In contrast on the 1n24 and 1n02 families $k_1$ and $k_3$ are through-bond whereas $k_2$, $k_3$ and $k_4$ are through-space. Therefore, one expects $k_1 > k_3 > 0$ and $k_1 > k_2$, but in many materials one will find that $k_2 < k_3 < k_4 < 0$. We show below that these differences are responsible for the different antiferroelastic orders observed in the 1n14, 1n24, and 1n02 families.

Results and Discussion

To understand the zero-temperature phase diagrams, Fig. 4 it is helpful to consider which ordering patterns minimise the interactions individually. The nearest-neighbour interaction is minimised by Néel order (Fig. 1a) for $k_1 > 0$ and by ferroelastic order (i.e., the HS or LS phases) for $k_1 < 0$. The second nearest-neighbour interaction is minimised by stripe order (Fig. 1b) for $k_2 > 0$ and by either ferroelastic or Néel order for $k_2 < 0$. The elastic interactions cooperate for $k_1 > 0$ and $k_2 < 0$, which are both minimised by Néel order, but are frustrated for any other parameters.

Both the long range strain and the single ion enthalpy favour ferroelasticity. These effects compete with the short-range elastic interactions to determine the ground state. If $J_\infty/(|k_1| \delta^2)$ and $\left| \Delta H/(|k_1| \delta^2) \right|$ are large then the ground state is either LS or HS, determined by the sign of $\Delta G$. While if $J_\infty/(|k_1| \delta^2)$ and $\left| \Delta H/(|k_1| \delta^2) \right|$ are small then either Néel or stripe ordering is thermodynamically stable.

With only nearest neighbour interactions, $k_1 > 0$, the HS, LS and Néel phases are degenerate at $\Delta G = 0$ (Fig. 4), and thermal fluctuations pick out Néel order at elevated temperatures (Fig. S14, section S3.1). However, with only nearest neighbour interactions present, the Néel phase is the only antiferroelastic phase present. Furthermore, the Néel phase is observed only in an extremely narrow temperature range. Experimentally, many different antiferroelastic phases have been found and these phases can be stable over relatively broad temperature ranges. This suggests that longer range elastic interactions are vitally important for multistep transitions.

Considering next nearest neighbour interactions, $k_1 > 0$ and $k_2 > 0$ is possible for any of the lattices shown in Fig. 2 provided that the minima of both interactions are roughly commensurate with a square lattice. At $T = 0$ the LS and HS states are separated by a first order phase transition at $\Delta G = 0$, Figs. 4a and S15a. The frustration entirely suppresses the Néel order found at finite temperatures for $k_2 = 0$ (cf. Figs. S14 and S15).

For constant $\Delta H$, which represents individual materials, we find a single step transition (Fig. S15). Which can be sharp and first order, continuous, or a crossover, depending on the relative strengths of the elastic interactions and the single ion entropy (see section S3.2). Consistent with this prediction, single step transitions are common and observed in all of the families of materials discussed here.

One expects that many materials in 1n24 and 1n02 families will have ferroelastic next nearest neighbour interac-
tions ($k_2 < 0$, which requires $k_1 > 2|k_2|$). This leads to a much richer range of behaviours, Fig. 5. The Néel phase is stable at $T = 0$ and there are two lines of first order transitions ending at two critical points Fig. 5a. For individual materials with fixed $\Delta H$ this leads to seven thermodynamically distinct behaviours. Generically, there is a two step transition from HS to Néel to LS as the temperature is lowered. Each step can be either a crossover, a first order transition or a second order transition.

If the single ion enthalpies of the HS and LS states are finely balanced (small $|\Delta G/(|k|\delta T)|$) then there is a first order, one step, incomplete transition between the Néel ordered phase and the HS phase (Figs. 3b-c, S6b-c and S13e). An incomplete one-step transition is even observed when $\Delta H$ is small and negative, Figs. 5a and S6b. This is remarkable as the single ion free energy, $\Delta G$, favours the HS state at all temperatures. This transition is a truly collective effect driven by the system’s need to minimise the energy of the elastic interactions, which are strong in this regime, in order to minimise the total free energy of the system.

In some cases the hysteresis is sufficiently broad that straightforwardly cooling the system does not achieve the true low temperature ground state. This is observed experimentally and has been called ‘hidden hysteresis’. Nevertheless it may be possible to prepare the ground state either via the reverse LIESST effect or by applying and subsequently adiabatically releasing pressure.

For larger $\Delta G/(|k|\delta T)$ both steps are straightforwardly observable and show significant hysteresis (Figs. 5c and S6e). The width of the hysteresis loops decrease as $\Delta G/(|k|\delta T)$ increases. The low temperature step always displays wider hysteresis than the high temperature step. On further increasing $\Delta G/(|k|\delta T)$ first the high temperature step passes through the critical point and becomes a crossover, with the low temperature step remaining first order and hysteretic (Figs. 5d and S6f). Then the lower temperature step passes through the critical point and becomes a crossover (Figs. 5g and S6g). There are no parameters for which the high temperature step is first order and the low temperature step is a crossover (cf. Fig. 5h). For sufficiently large $\Delta G/(|k|\delta T)$ the elastic interactions become unimportant and the temperature dependence of $n_{HS}$ begins to resemble a single crossover (Figs. 5i and S6i). The distinction between the two crossovers and single crossover regimes is much clearer in the heat capacity, Fig. S6, than in $n_{HS}$.

In all of these cases, the phase with $n_{HS} \simeq 1/2$ is Néel ordered. The Néel phase is found experimentally in many materials in the 1n24 and 1n02 families, and also in supramolecular crystals. Both as the intermediate spin-state in two-step transitions, and as the low temperature phase in incomplete one-step transitions.

One expects that for many 1n14 materials $k_1 < 0$ and $k_2 > |k_1|/2$. This leads to antiferroelastic states with stripe order (Figs. 3a and 3b). Apart from this important difference, the thermodynamic behaviour is extremely similar to that predicted for the 1n24 and 1n02 families ($k_1 > 0$, $k_2 < 0$; Figs. 5 and S6). Both the Néel and stripe phases have $n_{HS} = 1/2$. In both cases we observe two lines of first order transitions ending in two critical points (compare Fig. 5b to 5a). This gives rise to the same range of possible behaviours for individual materials (fixed $\Delta H$) as we found on the 1n24 family and 1n02 families: compare Figs. 5 and S6 to 3 and 8.

Stripe order has been observed in many 1n14 frameworks, and also in supramolecular crystals. Both as the low temperature phase in an incomplete first-order transition, and as the intermediate phase in two-step transitions, just as we find in our calculations.

Néel ordering is commonly found as an intermediate spin-state in the 1n24 and 1n02 families while, stripe ordering is common in the 1n14 family. Our calculations therefore give a clear explanation for this structure-property relationship. In the 1n24 and 1n02 families one expects the $k_1$ interactions to be strong and antiferreelas-
Figure 6: (a) Typical phase diagram for the next nearest neighbour model of the 1n14 family with $k_1 < 0$ and $k_2 > 0$ (here $k_2 = 1.2|k_1|$; see also Fig. S7). (b-f) The fraction of high spins, $n_{HS}$ (see Fig. S8 for the corresponding heat capacities). Symbols have the same meanings as in Fig. 5. In contrast to the 1n24 and 1n02 families (Fig. 5) the antiferroelastic order is striped (Fig. 3) rather than Néel (Fig. 4).

While Fig. 7 is typical of the rich behaviour of the third nearest neighbour model, the behaviours displayed there are far from exhaustive of this model. In Figs. S10a-c (and Figs. S10b-c) we show some additional examples of two-, three-, and four-step transitions with $k_1 > 0$, $k_2 < 0$ and $k_3 > 0$ (relevant to the 1n24 and 1n02 families). Importantly the antiferroelastic order can vary with the Néel phase competing with the E and G phases at $n_{HS} = 1/2$. D phases are often stable for $n_{HS} = 1/3$ or 2/3 in this parameter regime. Although we only show a single temperature trace for each case we emphasise that for each case varying $\Delta H$ results in the same range of thermodynamic behaviours as we saw in Fig. 4 with incomplete transitions, first order transitions, second order transitions, and crossovers observed.

Some of the phenomenology found here has been reported in experimental literature, for example Clements et al. [12] reported a four-step transition with intermediate plateaus at $n_{HS} = 2/3$, 1/2, and 1/3 in [Fe(bipytz)(Au(CN)$_2$)$_2$]$_x$·x(EtOH), which is in the 1n24 family. They demonstrated that the antiferroelastic order in these plateaus is D$_f$, Néel, and D$_L$ respectively. This is precisely the behaviour shown in Fig. S10 (and Fig. S10d).

For the 1n14 family one expects $k_2 > 0$ and, in many materials, $k_1 < 0$ and $k_3 < 0$. In this regime we observe
Figure 7: (a) Typical slice of the phase diagram for the third nearest neighbour model of the 1n24 and 1n02 families with $k_1$ and $k_3 > 0$, and $k_2 < 0$ (here $k_2 = -0.9k_1$ and $k_3 = 0.5k_1$). (b-i) The fraction of high spins, $n_{HS}$ (see Fig. S9 for the corresponding heat capacities). For simplicity we only show the parallel tempering Monte Carlo predictions. Symbols have the same meanings as in Fig. 5.

Figure 8: Examples of the wide range of behaviours found in the third nearest neighbour model. Here we study parameters relevant to (a) the 1n14 family, (b,c,d,e) the 1n24 and 1n02 families and (a-j) supramolecular lattices. Only the parallel tempering Monte Carlo simulations are shown. The intermediate spin-state phases are labelled on the plots (cf. Fig. 1). The corresponding heat capacities are shown in Fig. S10.
only one- and two-step transitions. The latter with intermediate stripe order similar to the transitions reported in Fig. 6. However, one also expects that in some materials \( k_1 > 0 \). In this regime we find a four-step transition with intermediate \( n_{HS} = 1/4 \) (C\(_L\)), 1/2 (stripe) and 3/4 (C\(_H\)) plateaus (Figs. S8a and S10a).

Many materials in the all families will have \( k_1 > 0 \), \( k_2 > 0 \), and \( k_3 > 0 \). In this case the long-range strain \( (J_{ss}) \) dominates over the elastic interactions. This allows only one-step transitions.

For supramolecular crystals the only constraint on the parameters is that the lattice is stable (i.e., that \( J_\infty = 4(k_1 + 2k_2 + 4k_3) > 0 \)). This allows for an even greater range of possibilities. Some of these are demonstrated in Figs. S5-j and S10a-j. We see four-step transitions with a variety of different antiferroelastic orders and fractions of HS in the intermediate plateaus. Similar to the previous cases studied, varying \( \Delta H/(k_3 \delta^2) \) can lead to incomplete transitions, first order transitions, second order transitions and crossovers. Several of these behaviours have been reported in the experimental literature. For example, two step transitions with intermediate stripe phases have been reported by Hang et al., Vieira et al., Chernyshov et al., Klingele et al., Fitzgerald et al. and a two-step incomplete transition with a low temperature stripe and intermediate \( C_H \) \( (n_{HS} = 0.75) \) antiferroelastic states has been reported by Matsumoto et al. Overall the third nearest neighbour model suggests that longer range elastic interactions lead to a wider range of behaviours. This includes transitions with a greater number of steps and a greater variety of antiferroelastic order.

Forth nearest neighbour interactions are through-space in the 1n14, 1n24 and 1n02 families, thus one might expect it to be weak in all classes of materials. However, \( k_5 \) is through-space in the 1n24 and 1n02 families but through-bond in the 1n14 family. Thus, we expect \( k_5 \) to be positive in 1n14 family materials. Therefore, to test our proposal that longer range interactions generically increase the number of plateaus in SCO materials we study our model with \( k_4 = 0 \) and non-zero \( k_1, k_2, k_3 \) and \( k_5 \).

For materials in the 1n14 family one expects \( k_2 > 0 \) and \( k_5 > 0 \), but for many materials \( k_1 < 0 \) and \( k_3 < 0 \). This leads to stable states consistent with plateaus at \( n_{HS} = 1 \) (HS), \( \frac{2}{3} \) (R\(_H\)), \( \frac{1}{3} \) (R\(_L\)), or 0 (LS), Fig. S18a. Other than the change in the antiferroelastic order the behaviours are extremely similar to those shown in Fig. 4 where we also find plateaus at the same HS fractions. The five phases are separated by four first order lines ending at critical points. Once again, for smaller values of \( \Delta H/(k_1 \delta^2) \) the transitions are sharp and first order, broadening for increasing values until the transitions become crossovers (see Figs. S18b-j and S11b-j).

The inclusion of the \( k_5 \) interaction also allows for a large number of possible antiferroelastic states and an extremely rich phase diagram, Fig. S17. At \( T = 0 \) we have identified 36 possible ground states that are stabilised in extended regions of the phase diagram, Fig. 1. For parameters relevant to 1n14 family \( (k_2 > 0 \text{ and } k_5 > 0) \) the HS, LS, stripe (B), C, J, K, R, S, and I phases are predicted. For parameters relevant to 1n24 and 1n02 families \( (k_1 > 0 \text{ and } k_3 > 0) \) the HS, LS, Néel (A), stripe (B), C, D, E, F, G, L, M, N, O, and P phases are found. Once again, this is consistent with experimental literature, where R\(^{13}\) and R\(^{13}\) phases have been reported for materials in the 1n14 family; and D\(^{14}\), \(^{20}\) and P\(^{14}\), \(^{19}\) \(^{22}\) phases have been observed in materials in the 1n24 family.

The diversity of the phases, Fig. 9a, leads to a very large numbers of steps. For example, in Fig. 9b (and Fig. S12b) we report an eight-step transition, for parameters relevant to 1n24 and 1n02 families. In the final stages of preparing this manuscript we became aware of an eight step transition reported recently by Peng et al.\(^2\) for a 1n24 material.

As in the previous cases, increasing \( \Delta H/(k_1 \delta^2) \) increases the widths of the transitions, and eventually causes the them to become crossovers. This starts with the highest-temperature transitions and works progressively down (see Figs. 6b-e). For large \( \Delta H/(k_1 \delta^2) \) the crossover becomes extremely smooth as it passes through all nine phases (see Figs. 9 and S12f). Thus, \( n_{HS} \), does not show any significant differences from a trivial single crossover. However, clear signatures are still observed in the \( CV \) and \( \partial n_{HS}/\partial T \), see Fig. S12. Unless the heat capacity or \( \partial n_{HS}/\partial T \) is measured this highly-multi-step crossover could be broadly dismissed as a single broad crossover. This means that extremely multistep SCO crossovers may hidden in plain sight in the literature. It is interesting to note that while, for these two-dimensional lattices increasing the number and range of interactions leads to transitions with an increasing numbers of steps, in the one dimensional Ising model only next nearest interactions are required to see an infinite number of steps (Devil’s staircase).\(^{33} \), \(^{54}\)
Conclusion

The simple elastic model explored here hosts a rich variety of SCO transitions and intermediate spin-state phases. Several of the SCO phases found here have been reported experimentally. This includes the Néel (A), stripe (B), D, T phases. This emphasizes that the range of the elastic phenomena in SCO materials.

We have established clear structure-property relations for the 1n14, 1n24 and 1n02 families of SCO materials. The key point is that through-bond elastic interactions are generically antiferroelastic (described by positive spring constants) whereas through-space elastic interactions can often be ferroelastic (negative spring constants). This provides a natural explanation for the different antiferroelastic phases found in different families of SCO frameworks.

In general, increasing the range of interactions results in an increase in the number of observed transitions and spin-state phases. Therefore, the rigidity of framework materials may explain why they are such a rich playground for multistep transitions and antiferroelastic order.

The inclusion of up to fifth nearest neighbour elastic interactions allows for eight-step transitions for parameters relevant to the 1n24 and 1n02 families. This suggests that transitions with larger numbers of steps could be obtained more readily in the 1n24 and 1n02 families than in the 1n14 family.

Further insight into these trends could be gained by parametrising our model for specific materials. However, this remains a major challenge.

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The lattice is stable to shear distortions because the symmetric breathing mode approximation is equivalent to assuming an infinite spring constant for shear modes.
SUPPLEMENTARY INFORMATION

S1 DETAILS OF THE MODEL

We start from the free energy difference, $\Delta G^1$, of a single metal centre undergoing spin crossover (SCO):

$$\hat{H}_0 = \frac{1}{2} \sum_i (\Delta H_i - T \Delta S) \sigma_i = \frac{\Delta G^1}{2} \sum_i \sigma_i,$$

(4)

where $\Delta H_1 = H_H - H_L$ and $\Delta S = S_H - S_L$ are the enthalpy and entropy differences between isolated HS and LS metal centres respectively. Following Wajnflasz and Pick, we have absorbed the single ion entropy difference into the local Hamiltonian. As discussed in the main text the entropy difference arises from changes in three microscopic terms: the spin and orbital degeneracies are different in the HS and LS states, and the vibrational entropy also changes due to the softening of the vibrational modes in the HS state. For example, for Fe$^{2+}$ metal centres in an octahedral complex, $\Delta S_{spin} = k_B \ln 5$ and $\Delta S_{orb} = k_B \ln 3$. Typically, the vibrational contribution is larger, such that $\Delta S \sim 4 \Delta S_{spin}$. Therefore, in all the calculations presented here we set $\Delta S = 4k_B \ln 5$. $\hat{H}_0$ describes spin crossovers in non- or weakly-interacting complexes, e.g., in solution. For $\Delta H_1 < 0$ the HS state is thermodynamically stable at all temperatures. While, for $\Delta H_1 > 0$ a LS state is realised at low temperatures, gradually undergoing a crossover to a HS state with equal numbers of HS and LS molecules at $T_{1/2} = \Delta H_1/\Delta S$.

In the solid state, cooperative elastic interactions between metal centres can lead to first-order phase transitions and hence hysteresis. If the neighbouring metal centres are connected through strong covalent bonds then one expects that the potential is close to its minimum and thus the harmonic approximation is reasonable. This justifies modelling the material as a network of springs. However, when multiple competing interactions are present it may not be possible to minimize all of the interactions simultaneously – i.e., there is frustration in the system. Paez-Espejo et al. described this by introducing a ‘frustration parameter’, which measures the extent to which different interactions are minimized by different structures. A problem with this approach is that weaker interactions, particularly through-space interactions, may be far from their minima. This is important because the harmonic approximation for molecular vibrations, which is implicit in Paez-Espejo et al.’s formalism, is only valid near the minimum of the potential. Here we introduce an approach that removes that difficulty.

We consider an inter-metal center potential, $V(r)$, that is an arbitrary function of the separation between the metal centres, $r$. Because the HS and LS phases have different crystal structures the equilibrium distance between nearest neighbour SCO ($M$) sites, $r_0$, will be different in the two phases. We write $r_0 = r_H$ in the HS phase and $r_0 = r_L$ in the LS phase. Thus, in either phase:

$$r_0 = \overline{R} + \delta (\sigma_1 + \sigma_2),$$

(5)

where $\overline{R} = (r_H + r_L)/2$ and $\delta = (r_H - r_L)/4$. For simplicity we assume that Eq. (5) holds in antiferroelastic phases as well. On noting that $\sigma_1^2 = 1$ because $\sigma_i = \pm 1$, we can write any function of the spin-states of the metal ions, $\sigma_i$ and $\sigma_j$, in the form

$$V_{ij}(r, \sigma_i, \sigma_j) = g_{ij}(r) + h_{ij}(r) [r - \eta_{ij} \{\overline{R} - \delta (\sigma_i + \sigma_j)\}] + \frac{1}{2} k_{ij}(r) [r - \eta_{ij} \{\overline{R} - \delta (\sigma_i + \sigma_j)\}]^2,$$

(6)

where $\eta_{ij} = \eta_n = 1, \sqrt{2}, 2, \sqrt{5}, 2\sqrt{5}, \ldots$ is the ratio of distances between the $n$th and 1st nearest-neighbour distance on the undistorted square lattice.

We interpolate $V_{ij}(r, \sigma_i, \sigma_j)$ by introducing a new function $V_{ij}(r)$ defined such that $V_{ij}(r_H) = V_{ij}(r_H, 1, 1)$, $V_{ij}(r_L) = V_{ij}(r_L, -1, -1)$, and $V_{ij}(\overline{R}) = V_{ij}(\overline{R}, 1, -1) = V_{ij}(\overline{R}, -1, 1)$, which yields

$$g_{ij}(r) = V_{ij}(r - \overline{R} \eta_{ij}) - (r - \overline{R} \eta_{ij}) \left( \frac{V_{ij}(r - \overline{R} \eta_{ij} + 2 \delta \eta_{ij}) - V_{ij}(r - \overline{R} \eta_{ij} - 2 \delta \eta_{ij})}{4 \delta \eta_{ij}} \right),$$

(7)

$$h_{ij}(r) = \frac{1}{2} (r - \overline{R} \eta_{ij})^2 \left( \frac{V_{ij}(r - \overline{R} \eta_{ij} + 2 \delta \eta_{ij}) - 2 V_{ij}(r - \overline{R} \eta_{ij}) + V_{ij}(r - \overline{R} \eta_{ij} - 2 \delta \eta_{ij})}{(2 \delta \eta_{ij})^2} \right),$$

and

$$k_{ij}(r) = \frac{V_{ij}(r - \overline{R} \eta_{ij} + 2 \delta \eta_{ij}) - 2 V_{ij}(r - \overline{R} \eta_{ij}) + V_{ij}(r - \overline{R} \eta_{ij} - 2 \delta \eta_{ij})}{(2 \delta \eta_{ij})^2}.$$
Noting that
\[ V(r - \mathbf{R}_{ij} + 2\delta \eta_{ij}) = \sum_{n=0}^{\infty} V^{(n)}(r - \mathbf{R}_{ij}) \frac{(2\delta \eta_{ij})^n}{n!}, \]
where
\[ V^{(n)}(x) \equiv \left( \frac{\partial^n V(r)}{\partial r^n} \right) \bigg|_{r=x}, \]
we find, with no further approximation, that
\[ g_{ij}(r) = V_{ij}(r - \mathbf{R}_{ij}) - (r - \mathbf{R}_{ij}) \sum_{n=0}^{\infty} \frac{(2\delta \eta_{ij})^{2n}}{(2n+1)!} V^{(2n+1)}_{ij}(r - \mathbf{R}_{ij}) + \frac{(r - \mathbf{R}_{ij})^2}{2} V^{(2)}_{ij}(r - \mathbf{R}_{ij}) \]
\[ - (r - \mathbf{R}_{ij}) \frac{2(\delta \eta_{ij})^2}{3} V^{(3)}_{ij}(r - \mathbf{R}_{ij}) + \frac{(\delta \eta_{ij})^2}{6} V^{(4)}_{ij}(r - \mathbf{R}_{ij}) + \ldots \]
\[ h_{ij}(r) = \sum_{n=0}^{\infty} \frac{(2\delta \eta_{ij})^{2n}}{(2n+1)!} V^{(2n+1)}_{ij}(r - \mathbf{R}_{ij}) - 2(r - \mathbf{R}_{ij}) \sum_{n=1}^{\infty} \frac{(2\delta \eta_{ij})^{2(n-1)}}{(2n)!} V^{(2n)}_{ij}(r - \mathbf{R}_{ij}) \]
\[ = V^{(1)}_{ij}(r - \mathbf{R}_{ij}) - (r - \mathbf{R}_{ij}) V^{(2)}_{ij}(r - \mathbf{R}_{ij}) + \frac{2(\delta \eta_{ij})^2}{3} V^{(3)}_{ij}(r - \mathbf{R}_{ij}) - (r - \mathbf{R}_{ij}) \frac{(\delta \eta_{ij})^2}{3} V^{(4)}_{ij}(r - \mathbf{R}_{ij}) + \ldots \]
\[ k_{ij}(r) = 2 \sum_{n=1}^{\infty} \frac{(2\delta \eta_{ij})^{2(n-1)}}{(2n)!} V^{(2n)}_{ij}(r - \mathbf{R}_{ij}) \]
\[ = V^{(2)}_{ij}(r - \mathbf{R}_{ij}) + \frac{(\delta \eta_{ij})^2}{3} V^{(4)}_{ij}(r - \mathbf{R}_{ij}) + \ldots \]
It is convenient to write
\[ V_{ij}(r, \sigma_i, \sigma_j) = f_{ij}(r) + \delta \eta_{ij} h_{ij}(r)(\sigma_i + \sigma_j) + \frac{1}{2} k_{ij}(r) \left[ r - \mathbf{R}_{ij} - \delta \eta_{ij}(\sigma_i + \sigma_j) \right]^2, \]
where \( f_{ij}(r) = g_{ij}(r) + h_{ij}(r)(r - \mathbf{R}_{ij}) \). To leading order we can neglect the \( r \) dependence of parameters, setting
\[ f_{ij} = f_{ij}(\mathbf{R}_{ij}) = V_{ij}(\mathbf{R}_{ij}), \]
\[ h_{ij} = h_{ij}(\mathbf{R}_{ij}) = V^{(1)}_{ij}(\mathbf{R}_{ij}), \]
\[ k_{ij} = k_{ij}(\mathbf{R}_{ij}) = V^{(2)}_{ij}(\mathbf{R}_{ij}). \]
Now the term proportional to \( h_{ij} \) has the same functional form as \( \tilde{\mathcal{H}}_0 \) so we define \( \Delta H = \Delta H_1 + 4\delta \eta_{ij} \sum_j h_{ij} \) and \( \Delta G = \Delta H - T \Delta S \). Thus, we replace \( \tilde{\mathcal{H}}_0 \) by
\[ \mathcal{H}_0 = \frac{1}{2} \sum_i (\Delta H - T \Delta S) \sigma_i = \frac{\Delta G}{2} \sum_i \sigma_i. \]
This reflects the change in the lattice contribution to the total free energy when spin states change. However, it does not materially affect the calculations reported here as we do not calculate \( \Delta H \) for specific materials. The term proportional to \( k_{ij} \) is simply a harmonic interaction between the metal centres. Thus, the elastic interactions between metal centres can be represented by a network of springs even if the individual interactions are far from their minima.
To investigate spin-state transitions we model the elastic interactions between SCO active sites of the simple square lattice as a network of springs, illustrated in Fig. 2. We consider elastic interactions between \( n \)th nearest-neighbour metal centres
\[ \mathcal{H}_n = \frac{k_n}{2} \sum_{(i,j)} \left[ r_{ij} - \eta_n \left[ \mathbf{R} + \delta (\sigma_i + \sigma_j) \right] \right]^2 \]
where \( k_n \) is the spring constant between \( n \)th nearest-neighbour, \( (i,j)_n \) indicates the sum runs over all \( n \)th nearest-neighbours, and \( r_{ij} \) is the instantaneous distance between sites \( i \) and \( j \). We include interactions up to \( m \)th nearest-neighbour metal centres (we study \( m = 1 - 5 \)). Thus, the total Hamiltonian is
\[ \mathcal{H} = \sum_{n=0}^{m} \mathcal{H}_n. \]
S2 METHODS

To investigate the thermodynamic properties of Hamiltonian we employ Monte Carlo methods using single spin-flips and periodic boundary conditions with \( N = 60 \times 60 \) metal ions for the lattices. For each data point we take \( N \) measurements with steps of \( N \) points after equilibrating for \( 10N \) steps.

For each parameter set we performed three separate calculations: heating, cooling and parallel tempering. For the heating calculation, we initialize the simulation at the lowest temperature studied \((T = 0.01k_1\delta^2/k_B)\) in the \( T = 0 \) ground state predicted by analytic calculations; for higher temperature data points we seed the simulation with the spin-state output from the previous data point. Conversely, for the cooling run we initialize the calculations at the highest temperature studied in a random configuration, then use the resultant output state as a seed for the next data point. When using single spin-flip Monte Carlo the transitions can become frozen out at low temperatures leading to exaggerated predictions of the transition temperatures. We employ parallel tempering to find the lowest free energy state. For the parallel tempering calculations we initialize the simulation in a random configuration.

To calculate the heat capacity, \( c_V = c_V^c + c_V^s \), we consider both the single body contribution, \( c_V^c \), and the many body contribution, \( c_V^s \). The single body contribution comes from the contribution of the the single molecules to the entropy \( c_V^c = T(\partial S^s/\partial T) = T\Delta S(\partial n_{HS}/\partial T) \). Where, we have used a Savitzky-Golay filter to fit \( n_{HS} \) and thus calculate \( \partial n_{HS}/\partial T \). We calculate the many-body contribution from fluctuations in the true enthalpy \( c_V^s = ((E^2) - (E)^2)/(Nk_BT) \), where \( E = \mathcal{H} + (1/2)T\Delta S \sum \sigma_i \).

To construct the zero-temperature phase diagrams we analytically compared the energies of the spin-state phases found in the Monte Carlo calculations alongside a catalogue of possible phases.

S2.1 Symmetric breathing mode approximation

We make the ‘symmetric breathing mode approximation’, \( \mathcal{H} \), i.e., we assume that for all nearest neighbours, \( r_{i,j} = x \), and that the topology of the lattice is not altered by the changes in the spin-states. Thus, for longer ranged interactions, \( r_{i,j} = \eta_n x \). This is motivated by the expected quadratic energy cost for shear modes \( \mathcal{H} \) and the limit where the relevant spring constant is large. \( \mathcal{H} \)

We minimize the above model with respect to the instantaneous distance between nearest-neighbours \( x \). Expanding out the resultant Hamiltonian yields the effective Ising-Husimi-Temperley model in a longitudinal field

\[
\mathcal{H} \approx \sum_{n=1}^{m} J_n \sum_{(i,j)_n} \sigma_i \sigma_j - \frac{J_n}{N} \sum_{i,j} \sigma_i \sigma_j + \frac{\Delta G}{2} \sum_{i} \sigma_i,
\]

where, \( J_n = k_n n^2 \delta^2 \) is the effective interaction between of the \( n \)th closest-neighbour metal centres, \( J_{\infty} = \delta^2 \sum_{n=1}^{m} (k_n z_n n^2) \) is the long-range strain, \( z_n \) is the coordination number for \( n \)th nearest neighbours and \( N \) is the number of lattice sites. The long-range strain has equal strength between all metal centres, distributing the impact of local molecular volume changes due to spin-state transitions over the lattice. Minimization over the instantaneous bond distance requires that \((\partial^2 \mathcal{H})/(\partial x^2) = 2J_{\infty} > 0 \). Thus the crystal is dynamically unstable for \( J_{\infty} < 0 \), and therefore we do not study parameters in that regime below.

S3 ADDITIONAL RESULTS

In Figs. S23a, S24a, 5a, and 6a we show phase diagrams with lines indicating the limits of metastability on heating and cooling at fixed \( \Delta H \). The calculations which these lines are based on are shown in (Fig. S10, S12, S14 and S16).

In Figs. S23b-f, S24b-d, 5b-h, S17b-j, 8a-j, and S21b-f of the main text we report the fraction of high spins as \( n_h \) in the lattice. We show phase diagrams with lines indicating the limits of metastability on heating calculation, we initialize the simulation at the lowest temperature studied \((T = 0.01k_1\delta^2/k_B)\) in the \( T = 0 \) ground state predicted by analytic calculations; for higher temperature data points we seed the simulation with the spin-state output from the previous data point. Conversely, for the cooling run we initialize the calculations at the highest temperature studied in a random configuration, then use the resultant output state as a seed for the next data point. When using single spin-flip Monte Carlo the transitions can become frozen out at low temperatures leading to exaggerated predictions of the transition temperatures. We employ parallel tempering to find the lowest free energy state. For the parallel tempering calculations we initialize the simulation in a random configuration.

Lastly, in the main text we show the phase diagram for the next nearest neighbour 1n14 family lattice model with \( k_1 < 1, k_2 = 1.2|k_1| \) (Fig. 8, see also Fig. S17). In Fig. S22 we show phase diagram for the nearest neighbour model with \( k_1 < 1, k_2 = 0.6|k_1| \) demonstrating the importance of the relative contributions of the magnitudes of \( k_1 \) and \( k_2 \) on the thermodynamics.

S3.1 NEAREST-NEIGHBOUR INTERACTIONS

In this section, we consider only the nearest-neighbour elastic interaction, \( k_1 \). That is, we set \( k_2 = k_3 = k_4 = k_5 = 0 \). The stability of the lattice requires \( k_1 > 0 \). The phase diagram of this model is shown in Fig. S23a. As individual materials have constant \( \Delta H \), rather than constant \( \Delta G \), we mark lines of constant \( \Delta G \) on the phase diagram and report the thermodynamic properties at selected values of \( \Delta H \) (Figs. S23a-f). As individual materials have constant \( \Delta H \), rather than constant \( \Delta G \), we mark lines of constant \( \Delta G \) on the phase diagram and report the thermodynamic properties at selected values of \( \Delta H \) (Figs. S23a-f). As individual materials have constant \( \Delta H \), rather than constant \( \Delta G \), we mark lines of constant \( \Delta G \) on the phase diagram and report the thermodynamic properties at selected values of \( \Delta H \) (Figs. S23a-f). As individual materials have constant \( \Delta H \), rather than constant \( \Delta G \), we mark lines of constant \( \Delta G \) on the phase diagram and report the thermodynamic properties at selected values of \( \Delta H \) (Figs. S23a-f). As individual materials have constant \( \Delta H \), rather than constant \( \Delta G \), we mark lines of constant \( \Delta G \) on the phase diagram and report the thermodynamic properties at selected values of \( \Delta H \) (Figs. S23a-f).
Figure S10: The HS fraction, \( n_{HS} \), calculated on (a) cooling and (b) heating for the nearest neighbour square lattice model with \( k_1 > 0 \). Lines and dots have the same meanings as in Fig. S11a, where we show the full phase diagram.

Figure S11: (a) The phase diagram for nearest-neighbour interactions, \( k_1 > 0 \), reprinted from Fig. 4a for convenience. The colours indicate the equilibrium values for the fraction of high-spin metal centres, \( n_{HS} \), calculated via parallel tempering. We find a (black) line of first order transitions that bifurcates at a triple point and ends in two critical points (black dots). The blue (red) dashed line marks the limit of metastability for on the HS (resp. LS) phases on cooling (resp. heating), see Fig. S10. Individual materials have fixed \( \Delta H \) (not fixed \( \Delta G \)); the white lines are lines of constant \( \Delta H \) and their labels correspond to panels (b-f) where the heat capacity, \( C_V \), is plotted along these lines (see Fig. 4 for the corresponding high spin fractions). In these plots the blue, red and black lines represent the cooling, heating and equilibrium values respectively.

Figure S12: The HS fraction, \( n_{HS} \), calculated on (a) cooling and (b) heating for the next nearest neighbour square lattice model with \( k_2 = 0.1 k_1 > 0 \). Lines and dots have the same meanings as in Fig. S11a. See Fig. S13a for the full phase diagram.
Figure S13: (a) Phase diagram for the next nearest neighbour square lattice model with $k_2 = 0.1k_1 > 0$ reprinted from Fig. 6a for convenience. Lines and dots have the same meanings as in Fig. S11a. (b-d) The heat capacity, $c_V$, (see Fig. 6 for the corresponding HS fractions). Blue, red and black lines show data for the cooling, heating and thermal equilibrium predictions, respectively.

Figure S14: The HS fraction, $n_{HS}$, calculated on (a) cooling and (b) heating for the next nearest neighbour square lattice model with $k_1 > 0$ and $k_2 = -0.2k_1$, appropriate for the 1n24 and 1n02 families. Lines and dots have the same meanings as in Fig. S11a. See Fig. S15a for the full phase diagram.

Figure S15: Phase diagram for the next nearest neighbour square lattice model with $k_1 > 0$ and $k_2 = -0.2k_1$, appropriate for the 1n24 and 1n02 families, reprinted from Fig. 7a for convenience. Lines and dots have the same meanings as in Fig. S11a. (b-h) The heat capacity, $c_V$, (see Fig. 7 for the corresponding HS fractions). Blue, red and black lines show data for the cooling, heating and thermal equilibrium predictions, respectively.

Figure S16: The HS fraction, $n_{HS}$, calculated on (a) cooling and (b) heating for the next nearest neighbour square lattice model with $k_1 < 0$ and $k_2 = 1.2|k_1|$, appropriate for the 1n14 family. Lines and dots have the same meanings as in Fig. S11a. See Fig. S17a for the full phase diagram.
Figure S17: Phase diagram for the next nearest neighbour square lattice model with $k_1 < 0$ and $k_2 = 1.2|k_1|$, appropriate for the 1n14 family, reprinted from Fig. 8a for convenience. Lines and dots have the same meanings as in Fig. S11a. (b-h) The heat capacity, $c_V$, (see Fig. 8 for the corresponding HS fractions). Blue, red and black lines show data for the cooling, heating and thermal equilibrium predictions, respectively.

Figure S18: Phase diagram for the third nearest neighbour square lattice model with $k_1 > 0$, $k_2 = -0.9k_1$ and $k_3 = 0.5k_1$, appropriate for the 1n24 and 1n02 families, reprinted from Fig. 9a for convenience. Lines and dots have the same meanings as in Fig. S11a. (b-j) The heat capacity, $c_V$, (see Fig. 9 for the corresponding HS fractions). For simplicity only the parallel tempering results are shown.
Figure S19: Temperature dependence of the heat capacity in the third nearest neighbour model with the same parameters for which $n_{HS}$ is plotted in Fig. 10. The parameters are reasonable for (a) 1n14 family, (b-e) 1n24 and 1n02 families and (a-j) supramolecular lattices. For simplicity we only show the parallel tempering results.

Figure S20: Phase diagram for the fifth nearest neighbour square lattice model with $k_1 < 0$, $k_2 = 1.2|k_1|$, $k_3 = -0.5|k_1|$, $k_4 = 0$, and $k_5 = 0.2|k_1|$, appropriate for the 1n14 family, reprinted from Fig. 12a for convenience. Lines and dots have the same meanings as in Fig. S11a. (b-j) The heat capacity, $c_V$, (see Fig. S27 for the corresponding HS fractions). For simplicity only the parallel tempering results are shown.
In the opposite regime, $\Delta H \ll k_1 \delta^2$, we see a sharp one-step transition with hysteresis (Figs. S23b and S2b). This indicates a first order phase transition, as is commonly observed in bistable SCO materials. Note that in our calculations the first order spin-state transition is not accompanied by a crystallographic phase transition, which is excluded by the symmetric breathing mode approximation.

In the intermediate regime, $\Delta H/(|k_1|\delta^2) \sim 15 - 30$, we see two-steps. Depending on the magnitude of $\Delta H/(|k_1|\delta^2)$ these steps can occur as two first-order transitions with hysteresis (Figs. S23c and S2c), one first order transition and one crossover (Figs. S23d and S2d), or two crossovers (Figs. S23e and S2e). In between these regimes are critical points where the transitions become continuous.

The two-step behaviour is a result of the competition between the long-range strain and the elastic interactions. The elastic interactions favour an antiferroelastic phase with Néel ordering (Fig. 1a), whereas the long-range strain prefers all metal centres to be in the same spin-state. At $T = 0$ when $\Delta H = \Delta G > 0$ the LS phase is realized and for $\Delta H = \Delta G < 0$ the HS phase is energetically favourable. However, for $T = 0$ and $\Delta H = 0$ the Néel ordered state is degenerate with the HS and LS states (Figs. S23 and S1a). At sufficiently high temperatures thermal fluctuations stabilize the Néel ordered phase for $\Delta G \approx 0$, Figs. S23a and S2a, resulting in the observed two-step behaviours.

However, with only nearest neighbour interactions present, the Néel phase is the only antiferroelastic phase present. Furthermore, the Néel phase is observed only in an extremely narrow temperature range. Experimentally, many different antiferroelastic phases have been found and these phases can stable over relatively broad temperature ranges. This is consistent with the idea that longer range elastic interactions are vitally important for multistep transitions.

S3.2 STRICTLY POSITIVE NEXT NEAREST NEIGHBOUR INTERACTIONS (ANY FAMILY)

$k_1 > 0$ and $k_3 > 0$ is possible for any of the lattices shown in Fig. 2 provided that the minima of both interactions are roughly commensurate with a square lattice. At $T = 0$ the LS and HS states are separated by a first order phase transition at $\Delta G = 0$, Figs. 4a and S24a. For $T > 0$ this phase transition remains at $\Delta G = 0$ until it reaches a critical point, where the transition is continuous. Thus, the frustration has entirely suppressed the Néel order found at finite temperatures for $k_2 = 0$ (cf. Fig. S23 and S24).

Considering lines of constant $\Delta H$, which represent individual materials, we see three distinct thermodynamic behaviours: When the elastic interactions are strong compared to the single molecule physics, $\Delta H \ll |k_1|\delta^2$, the transitions are sharp and first-order, the width of the hysteresis is greater the smaller $\Delta H/(|k_1|\delta^2)$ is (Figs. S24b,c and S4b,c). If the elastic interactions are weak, $\Delta H \gg |k_1|\delta^2$, we find a crossover (Figs. S24d and S4d). These two regimes are separated by a continuous (or second order) phase transition at the critical point.

Consistent with this prediction, single step transitions are common and observed in all of the families of materials discussed here.
Figure S22: (a) Phase diagrams for the next nearest neighbour model with $k_1 < 0$, $k_2 > 0$ (here we take $k_2 = 0.6|k_1|$, other parameters give similar results). Lines and dots have the same meanings as in Fig. S11a. The HS fractions calculated on (b) heating and (c) cooling with fixed $\Delta H$ are used calculate the limits of stability. Note that in contrast to the results above (see, e.g., Figs. 8 and S17) lower the relative magnitudes of $k_1$ and $k_2$ has importance consequences for the observed behaviours. (d-j) The fraction of high spins, $n_{HS}$ and (k-q) the corresponding heat capacities. Blue, red and black lines show data for the cooling, heating and thermal equilibrium predictions, respectively.
Figure S23: (a) The phase diagram for nearest-neighbour interactions, $k_1 > 0$. Colours in the phase diagram indicate the fraction of high-spin $M$ sites, $n_{HS} \sim \chi T$ where $\chi$ is the susceptibility, calculated via parallel tempering. The (black) line of first order transitions bifurcates at a triple point and ends in two critical points (black dots). The blue (red) dashed line marks the limit of metastability for the HS (resp. LS) phases on cooling (resp. heating), cf. Fig. S1, and show the width of the hysteresis. Individual materials have fixed $\Delta H$, white lines correspond to panels (b-f), where the fraction of high spins is plotted (see Fig. S2 for the corresponding heat capacities). In these plots the blue, red and black lines represent the cooling, heating and parallel tempering values respectively.

Figure S24: (a) Typical phase diagram for the next nearest neighbour square lattice model with $k_1$ and $k_2 > 0$ (here $k_2 = 0.1k_1$; see also Fig. S3). (b-d) The fraction of high spins, $n_{HS}$ (see Fig. S4 for the corresponding heat capacities). Symbols have the same meanings as in Fig. S23.

Figure S25: Slices of the zero-temperature phase diagram with up to third nearest-neighbour elastic interactions $k_1, k_2$ and $k_3$ for (a,c) constant $\Delta H$ and (b,d,f-h) constant $J_\infty$. Grey lines in (a,c) indicate lines of constant $J_\infty$. In addition to the phases that are energetically preferred by individual elastic interactions (HS, LS, Néel, stripe, C, E and G), frustration introduces additional phases into the zero-temperature phase diagram (D, R and S). E, G indicates that the E and G phases are degenerate.
Figure S26: Selected slices of the zero temperature phase diagram with up to fifth nearest-neighbour interactions showing thirty-six distinct phases. In general increasing the number of nearest-neighbour interactions increases the complexity of the phase diagram.

Figure S27: (a) Typical phase diagram for the 1n14 family with $k_1 < 0$, $k_2 > 0$, $k_3 < 0$, $k_4 = 0$ and $k_5 > 0$ (here $k_2 = 1.2|k_1|$, $k_3 = -0.5|k_1|$ and $k_5 = 0.2|k_1|$). The R phase consists of alternating stripes of width 2 and width 1 (Fig. 1). Lines and dots have the same meanings as in Fig. S11a. (b-i) The fraction of high spins, $n_{HS}$ (see Fig. S20 for the corresponding heat capacities). Only the parallel tempering Monte Carlo predictions are reported.