

# A remarkable water-soluble (molecular) alloy with two tuneable solid-to-solid phase transitions

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The organometallic cations  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  are fully miscible in the solid state and form the mixed crystalline material  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_x\text{Fe}_{1-x}][\text{PF}_6]$ , which undergoes two fully reversible phase transitions that can be tuned by varying the molar ratio of the two cations; the water-soluble organometallic salt thus possesses the behaviour of a molecular alloy.

Crystal polymorphism is the property of a substance to exist in different crystalline phases resulting from different arrangements of the molecules in the solid state.<sup>1,2</sup> Polymorphic modifications of the same substance may differ markedly in chemical and physical properties such as diffraction pattern and solid state spectroscopy. We are investigating polymorphism and solid state dynamic behaviour in a systematic manner, with a focus on organometallic systems.<sup>3</sup> In particular, we are interested in obtaining new crystal forms by non-solution methods (*e.g.* grinding,<sup>4</sup> seeding,<sup>5</sup> desolvation<sup>6</sup>) and in controlling the interconversion between polymorphs and between pseudo-polymorphs. The study of polymorphism falls into the mainstream of (molecular) crystal engineering.<sup>7</sup>

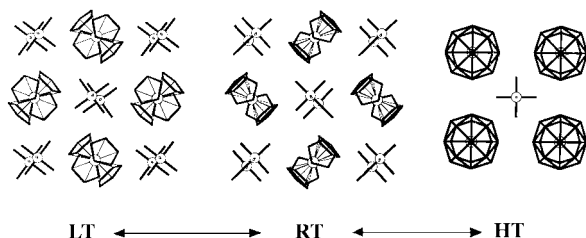
In this context, we have recently investigated by single crystal and powder X-ray diffraction as well as by calorimetric methods the phase transition behaviour of the crystalline salts  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}][\text{PF}_6]$  ( $\text{M} = \text{Co}, \text{Fe}$ ).<sup>8</sup> The two crystalline materials are isomorphous at room temperature and undergo two fully reversible solid-to-solid phase transitions on changing the temperature. A  $\text{RT} \rightleftharpoons \text{LT}$  transition occurs on cooling the room temperature phases below 252 ( $\text{M} = \text{Co}$ ) and 213 K ( $\text{M} = \text{Fe}$ ), whereas a  $\text{RT} \rightleftharpoons \text{HT}$  transition is observed on heating the crystalline materials above 314 ( $\text{M} = \text{Co}$ ) and 347 K ( $\text{M} = \text{Fe}$ ). Hence, the main difference between the two materials arises from the interval of thermal stability of the intermediate RT phase (*ca.* 62 K for  $\text{M} = \text{Co}$  and 134 K for  $\text{M} = \text{Fe}$ ). The relationship between the three solid phases is shown in Fig. 1.

The close structural similarity between the two complexes of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}]^+$  ( $\text{M} = \text{Co}, \text{Fe}$ ) prompted us to explore the possibility of growing crystals from solutions containing mixtures of the two cations. We were seeking answers to the

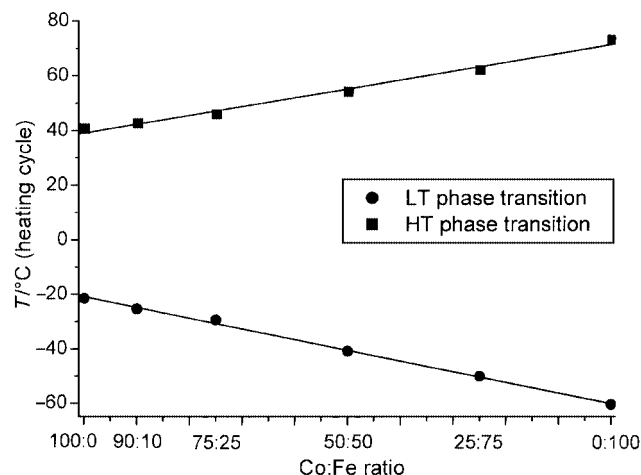
following questions: (i) would the two cations form co-crystals or separate out in crystals of the two salts? (ii) In the former case, could we expect to be able to control the phase transition behaviour by varying the  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+ : [(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  molar ratio? In this design we were also helped by the large difference in colour:  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{PF}_6]$  is bright yellow, and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{PF}_6]$  is deep blue.

We have discovered that, in the solid state, the two cations are fully miscible in the whole range of composition and that the composition is the same as that of the *water solutions* from which the mixed-crystals are precipitated, *e.g.* the mixed salts can be formulated as  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_x\text{Fe}_{1-x}][\text{PF}_6]$  (with  $0 < x < 1$ ). Moreover, the phase transition behaviour depends linearly on the composition. The temperatures at which the two solid-to-solid phase transitions occur vary regularly, as a direct function of the molar ratio, between the two extremes defined by the homo-cationic crystals.

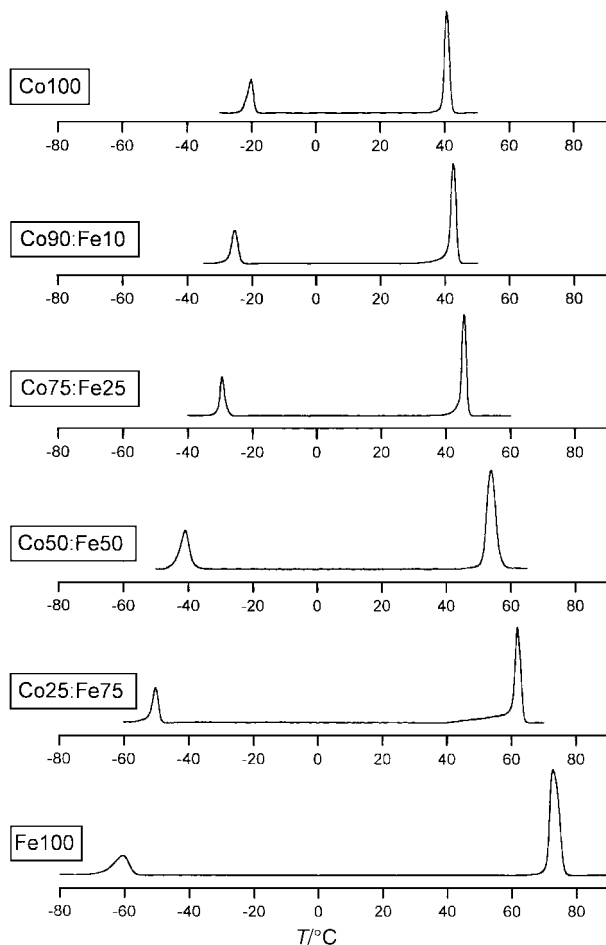
Mixed crystals were precipitated from water solutions containing  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+ : [(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  in the molar ratios: 90:10, 75:25, 50:50 and 25:75. The pure Co and Fe compounds have closely similar unit cell dimensions [data at room temperature for Co/Fe:  $a = 13.355(3)/13.408(6)$ ,  $b = 9.441(8)/9.530(2)$ ,  $c = 9.427(6)/9.482(2)$  Å,  $\beta = 92.87(4)/93.17(3)^\circ$ ,  $V_{\text{cell}} = 1187(1)/1209(1)$  Å<sup>3</sup>];<sup>8</sup> hence one could expect the mixed crystals to obey Vegard's rule of linear change in lattice dimensions with composition.<sup>9a</sup> Since deviations from this behaviour are known<sup>9b</sup> the diffraction patterns for all the bulk precipitates were measured to ensure that only the same phase as that of the starting materials had formed. The colours of the precipitates were also very indicative of the formation of mixed-crystals since  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_x\text{Fe}_{1-x}][\text{PF}_6]$  are green and the colour changes from green to



**Fig. 1** The relationship between the ion arrangements in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}][\text{PF}_6]$  ( $\text{M} = \text{Co}, \text{Fe}$ ) in their (a) low, (b) room and (c) high temperature phases; in the case of  $\text{M} = \text{Fe}$  also the anions are orientationally disordered in the high temperature phase.



**Fig. 2** The temperature variation of the  $\text{RT} \rightleftharpoons \text{LT}$  and  $\text{RT} \rightleftharpoons \text{HT}$  transitions with  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  in the molar ratios 100:0, 90:10, 75:25, 50:50, 25:75, 0:100.



**Fig. 3** DSC thermograms (heating cycle) showing how the  $RT \rightleftharpoons LT$  and  $RT \rightleftharpoons HT$  transitions 'diverge' from the values observed in the case of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$  as the percentage of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  in the mixture is increased. (For the sake of clarity and comparison, all baselines have been subtracted from the DSC thermograms.)

blue-green with the increasing molar fraction of the Fe component. Each mixed salt powder was subjected to a full cycle of differential calorimetry measurements (DSC), both in the cooling and in the heating regimes, to measure the temperatures of the two solid-to-solid phase transitions. The temperature variation of the  $RT \rightleftharpoons LT$  and  $RT \rightleftharpoons HT$  transitions with composition is shown in Fig. 2 (for the heating cycle). A comparison of the DSC thermograms is shown in Fig. 3: note how the peaks corresponding to the  $RT \rightleftharpoons LT$  and  $RT \rightleftharpoons HT$  transitions diverge as the percentage of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  is increased. As in the cases of the pure materials the two processes are fully reversible.<sup>10</sup>

In conclusion, we have been able to *tune* the phase transition behaviour of the crystalline material  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_x\text{Fe}_{1-x}][\text{PF}_6]$  by varying the  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+ : [(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  molar ratio, because the  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  cations form fully miscible solid solutions. The linear response of physical properties with composition is typical of inorganic alloys<sup>11</sup> and of crystals constructed by almost isostructural species (e.g. naphthalene and 1,2,4,5-tetrachlorobenzene, or 2-chloronaphthalene and 2-bromonaphthalene)<sup>11</sup> but, to the

best of our knowledge, it has never been reported for organometallic molecular salts. Thus, the mixed-crystal  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_x\text{Fe}_{1-x}][\text{PF}_6]$ , though being composed of molecular ions and soluble in water, possesses the features of a random  $A_xB_{1-x}$  alloy.

We plan to explore the behaviour of the salts  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{M}][\text{PF}_6]$  ( $M = \text{Co}, \text{Fe}$ ) on changing the counterions, *i.e.* by doping the crystals with isostructural anions such as  $[\text{AsF}_6]^-$  and  $[\text{SbF}_6]^-$ , and/or by using other isoelectronic, quasi-isomorphous, organometallic salts, *e.g.*  $[(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)\text{Ru}][\text{PF}_6]$  (one phase transition  $RT \rightleftharpoons HT$  at 332.5 K)<sup>12</sup> or  $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}][\text{PF}_6]$  (no phase transition between 200 and 373 K).<sup>8</sup>

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