

## Co-crystallisation of competing structural modes in geometrically constrained Jahn–Teller manganese(III) complexes†‡

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**The combination of Jahn–Teller distortion and chelating ligands produces a fine balance between competing coordination modes in manganese(III) resulting in well-ordered co-crystallization of two distinct assemblies from one set of components under a single set of conditions.**

The presence and direction of the Jahn–Teller (JT) axis plays a major role in the chemistry of manganese(III) both in biology<sup>1</sup> and materials.<sup>2</sup> In the majority of 6-coordinate manganese(III) complexes it is easily identified by an elongation along the *z* axis,<sup>3</sup> less commonly as an elongation along the *x* and *y* axes,<sup>4</sup> corresponding to population of the appropriate antibonding *d<sub>xy</sub>*<sup>2</sup> or *d<sub>x<sup>2</sup>−y<sup>2</sup></sub>* orbital in each case. In extended metal oxides the effect is locked into the oxide framework and the distortion may extend in more than one direction due to different orientation of the *d*-orbitals *via* a process termed orbital ordering which is important for transport properties.<sup>2,5,6</sup> In discrete molecular systems orbital ordering is not an issue but the ligand must be flexible enough to accommodate the distortion and when this is not possible the ion may be forced to adopt a new oxidation state. We have previously shown that ligand constraint can be harnessed to block access to the JT-distortion resulting in a range of oxidation state choices in manganese. This was demonstrated using a tris-imine, tris-phenolate N<sub>3</sub>O<sub>3</sub> donor set embedded in macrobicyclic or podand ligands with different bite angles. By tuning the level of constraint it was possible to stabilize manganese in its +II, +III and +IV oxidation states under ambient conditions.<sup>7</sup> In this way the system chose an electronic solution (redox change) to overcome a geometric constraint. We now show that a converse effect is also possible: namely that a geometric solution can be found for a strong electronic constraint, in this case a pronounced JT distortion in manganese(III), resulting in co-crystallisation of two competing structural modes with chelating ligands.

Possible coordination modes for a JT ion with tridentate chelating ligands include those where all donors coordinate or those where some are pushed off to accommodate the distortion by attachment of exogenous donors, Scheme 1. We report here the manganese(III) complexes of chelates L1–L3 which coordinate the high spin ion in competing but co-existing modes which co-crystallise into well-ordered frozen-out conformations of the (bis-tridentate) and (bis-bidentate + 2 exogenous L) arrangements.

The crystalline salts [Mn(L1)<sub>2</sub>][Mn(L1)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, **1**, [Mn(L2)<sub>2</sub>][Mn(L2)<sub>2</sub>(MeOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, **2**, and [Mn(L3)<sub>2</sub>][Mn(L3)<sub>2</sub>(EtOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, **3**, were recovered in good yield by room temperature addition of manganese(II) perchlorate to a solution of the appropriate Schiff base in alcohol/acetonitrile and standing for a few days in air.<sup>§</sup> All were X-rayed<sup>8</sup> to reveal well-ordered co-crystallization of a *facially* coordinated bis-tridentate Mn(III) site (site 1) alongside a bis-bidentate ion with two exogenous solvent molecules in the axial positions (site 2), Fig. 1–3. In all three complexes the asymmetric unit comprises two half occupancy manganese complex cations on inversion centres and one full occupancy perchlorate anion.

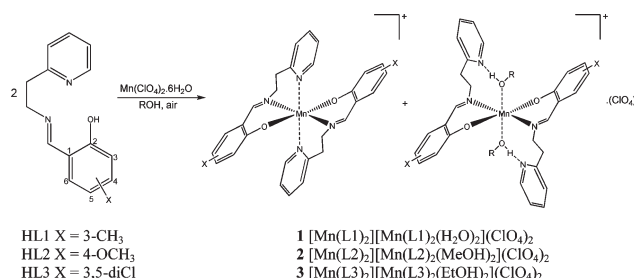
The coordination around manganese in each site is *pseudo*-octahedral with a pronounced Jahn–Teller elongation and the most striking feature in site 1 for each of complexes **1–3** is the unusually long Mn–N<sub>pyridine</sub> bond length, which varies from 2.33–2.37 Å, Table 1. These are amongst the longest known in both manganese(III) mononuclear<sup>9</sup> and cluster<sup>10</sup> complexes. However all the reported mononuclear examples contain an equatorially constrained tetradentate donor set which seems to force a stretch of the bonds along the *z* axis which is not the case for **1–3**. It is also noteworthy that there is a significant loss of planarity in the bonding between the pyridine ring and Mn, and

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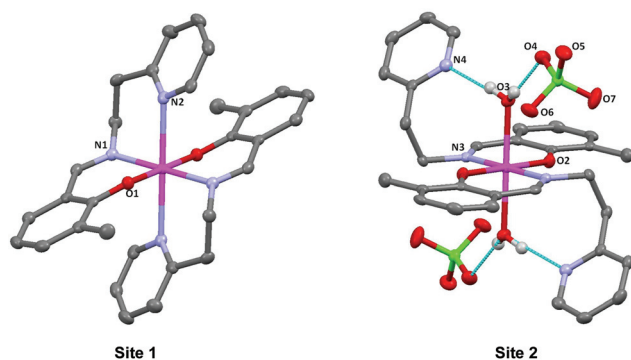
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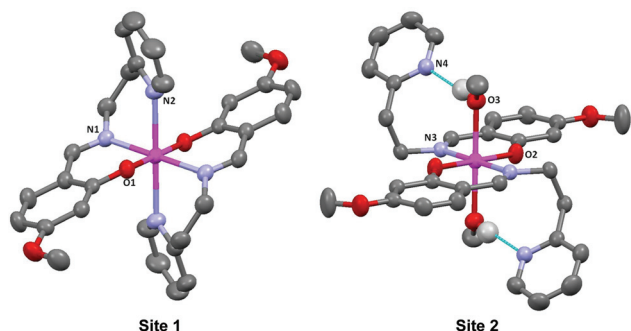
‡Electronic supplementary information (ESI) available. CCDC 718584, 718586, 718585. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31742g



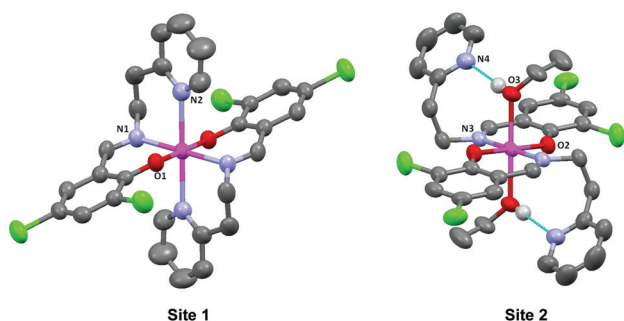
**Scheme 1** Assembly *via* two coordination modes from tridentate ligands L1–L3 with manganese(III).



**Fig. 1** View of two cations in  $[\text{Mn}(\text{L}1)_2][\text{Mn}(\text{L}1)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ , **1**, showing [bis-tridentate] (site 1) and [bis-bidentate + two exogenous ligand] (site 2) modes with two exogenous aqua ligands. All hydrogen atoms save those on the coordinated water molecules are omitted for clarity. Relative orientation of two sites not shown here.



**Fig. 2** View of two cations in  $[\text{Mn}(\text{L}2)_2][\text{Mn}(\text{L}2)_2(\text{MeOH})_2](\text{ClO}_4)_2$ , **2**, showing [bis-tridentate] (site 1) and [bis-bidentate + two exogenous ligand] (site 2) modes with two exogenous methanol ligands. Counterions and hydrogen atoms save those on the methanol donors omitted for clarity. Relative orientation of two sites not shown here.



**Fig. 3** View of two cations in  $[\text{Mn}(\text{L}3)_2][\text{Mn}(\text{L}3)_2(\text{EtOH})_2](\text{ClO}_4)_2$ , **3**, showing [bis-tridentate] (site 1) and [bis-bidentate + two exogenous ligand] (site 2) modes with two exogenous ethanol ligands. Counterions and hydrogen atoms save those on the ethanol donors omitted for clarity. Relative orientation of two sites not shown here.

there is a clear correlation between  $\text{Mn}-\text{N}_{\text{pyridine}}$  length and loss of planarity which is most likely due to the nature of the substitution on the phenolate ring: The strongly electron donating methyl groups in **1** strengthen the  $\text{Mn}-\text{O}_{\text{phen}}$  bond leading to a larger energy gap between the bonding and anti-bonding orbitals.  $\text{Mn}-\text{N}_{\text{pyridine}}$  is consequently longer and the aromatic ring

**Table 1** Bond lengths ( $\text{\AA}$ ) and distortion angles ( $^\circ$ ) for sites 1 and 2 in complexes **1–3**

	$\text{Mn}-\text{N}_{\text{pyridine}}$	$\text{Mn}-\text{N}_{\text{imine}}$	$\text{Mn}-\text{O}_{\text{phen}}$	$\text{Mn}-\text{pyridine bend}$
Site 1				
1	2.374(2)	2.022(2)	1.871(2)	154.1(1)
2	2.329(1)	2.041(1)	1.884(1)	162.97(8)
3	2.326(2)	2.015(2)	1.889(2)	173.7(1)
	$\text{Mn}-\text{O}_{\text{solvent}}$	$\text{Mn}-\text{N}_{\text{imine}}$	$\text{Mn}-\text{O}_{\text{phen}}$	
Site 2				
1	2.251(2)	2.034(2)	1.877(2)	
2	2.247(1)	2.040(1)	1.878(1)	
3	2.243(2)	2.048(2)	1.864(2)	

bends out of plane to accommodate the stretch; the effect is reversed with electron-withdrawing groups as in **3**.

The alternative bonding mode of (bis-bidentate + 2 exogenous L) is trapped at site 2 where the axial positions are filled by coordinating solvent while the pyridine donor has been pushed off by the Jahn–Teller stretch. The coordinated solvent fastens on to the pyridine nitrogen by hydrogen bonding in each case assisting the chelate effect by holding the N-donor in close proximity where it can re-attach to the metal ion with ease. In complex **1** the coordinated water molecule forms a second hydrogen bond to the perchlorate counterion, Fig. 1.

This result is reminiscent but distinct from examples of coordination isomerism such as the well-known example of different geometries for pentacyanonickelate(II),<sup>11</sup> in that the two sites in **1–3** are *not* isomeric and in fact have different donor sets:  $\text{N}_4\text{O}_2$  at site 1 and  $\text{N}_2\text{O}_4$  at site 2. It is also distinct from examples where different assemblies from one set of components can be obtained under different crystallization conditions.<sup>12</sup> The unusual aspect here is that two quite different coordination complexes assemble from one set of components and are sufficiently equi-energetic to co-crystallise in attempts with three different ligands L1–L3. The crystallisation of both modes points to equi-energetic or close to equi-energetic potential wells for both arrangements. Metallosupramolecular chemistry is founded on the principles of programmed self-organisation of a single assembly<sup>13</sup> from one set of organic components around a metal ion with well defined geometric preferences.<sup>14</sup> Here introduction of two competing effects generates the supramolecular equivalent of a “molecule in distress”<sup>15</sup> which results in two structural minima and two output assemblies from one set of molecular components under the same conditions, Scheme 1. Our system therefore represents a trap for the dynamic equilibrium expected for a metal–ligand assembly in solution as introduction of Jahn–Teller distortion upsets the balance of the expected weighting toward maximum chelate coordination, generating a finely poised co-existence of the two assemblies. This may find useful application in catalysis and work is underway to explore the potential of this labile coordination site.

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## Notes and references

§ Typical synthesis: To a well stirred solution of 2-(2-aminoethyl)-pyridine (0.244 g; 2.0 mmol) in a 50:50 acetonitrile–alcohol solvent (50 mL) was added the appropriate substituted salicylaldehyde (2.0 mmol). The resulting bright yellow-coloured solution was stirred at room temperature for 15 minutes before solid manganese(II) perchlorate hexahydrate (0.362 g; 1.0 mmol) was added to the reaction. A brown colour developed and the mixture was stirred at room temperature for 30 minutes after which time the solution was gravity filtered. Crystals were grown from the filtrate or from recrystallisation of the powder from acetonitrile/alcohol.

Elemental analysis (%):  $[\text{Mn}(\text{L}1)_2(\text{H}_2\text{O})_2][\text{Mn}(\text{L}1)_2(\text{ClO}_4)_2]$ , **1**: calc for  $\text{C}_{60}\text{H}_{64}\text{N}_8\text{O}_{14}\text{Cl}_2\text{Mn}_2$  C 55.35, H 4.55, N, 8.61; found C 55.17, H 5.01, N 8.42;  $\mu = 4.85 \mu_{\text{B}}$  (80 K),  $\mu = 4.81 \mu_{\text{B}}$  (280 K);  $[\text{Mn}(\text{L}2)_2(\text{MeOH})_2][\text{Mn}(\text{L}2)_2(\text{ClO}_4)_2]$ , **2**: calc for  $\text{C}_{62}\text{H}_{68}\text{N}_8\text{O}_{18}\text{Cl}_2\text{Mn}_2$  C 53.42, H 4.92, N 8.04; found C 53.45, H 4.90, N 7.98;  $\mu = 4.93 \mu_{\text{B}}$  (80 K); 4.92 (280 K);  $[\text{Mn}(\text{L}3)_2][\text{Mn}(\text{L}3)_2(\text{EtOH})_2][\text{ClO}_4)_2]$ , **3**: calc for  $\text{C}_{60}\text{H}_{56}\text{N}_8\text{O}_{14}\text{Cl}_{10}\text{Mn}_2$ : C 45.68, H 3.58, N, 7.10; found C 45.46, H 3.60, N 6.94;  $\mu = 4.91 \mu_{\text{B}}$  (80 K); 4.87 (280 K).

Magnetic susceptibility was measured between 80 and 300 K on a Faraday Balance calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$ . Experimental susceptibilities were corrected for diamagnetism of the constituent atoms using Pascal's constants. Crystal data for **1–3** were collected on a Bruker SMART APEX CCD area detector diffractometer and X-ray pictures were generated using Mercury.<sup>16</sup>

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- 8 Crystal data for **1** (100(2) K):  $0.8 \times 0.5 \times 0.4 \text{ mm}^3$ ; monoclinic;  $P2_1/n$ ;  $a = 11.041(2)$ ,  $b = 22.468(4)$ ,  $c = 11.656(2) \text{ Å}$ ,  $\beta = 95.026(2)^\circ$ ,  $U = 2880.48(9) \text{ Å}^3$ ;  $\rho_{\text{calcd}} = 1.501 \text{ Mg m}^{-3}$ ;  $2\theta_{\text{max}} = 52.00^\circ$ ; Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ Å}$ );  $\phi-\omega$ -scans; 23 011 reflections collected, 5654 independent (all included in refinement); correction for Lorentzian polarization and absorption: Semi-empirical from equivalents (program SADABS;<sup>17</sup>  $\mu = 0.607 \text{ mm}^{-1}$ , max. and min. transmission 0.7934 and 0.5892); solution: direct methods ((SHELXS-97<sup>17</sup>); refinement: Full-matrix least-squares against  $|F^2|$  (SHELXL-97-2<sup>17</sup>), 401 parameters; hydrogen atoms attached to oxygen were located in the difference Fourier map and allowed to refine freely, all other hydrogen atoms were added at calculated positions and refined using a riding model;  $R_1 = 0.060$ ,  $wR_2 = 0.113$  (all data); max/min residual electron density:  $0.64/-0.50 \text{ e}^-/\text{Å}^3$ ; deposited at the Cambridge Crystallographic Data Centre, no. CCDC 718584. Crystal data for **2** (293(2) K):  $1.0 \times 1.0 \times 0.8 \text{ mm}^3$ ; triclinic;  $P\bar{1}$  (#2);  $a = 10.0933(7)$ ,  $b = 10.5813(8)$ ,  $c = 15.0387(11) \text{ Å}$ ,  $\alpha = 87.740(1)^\circ$ ,  $\beta = 85.350(1)^\circ$ ,  $\gamma = 84.701(1)^\circ$ ,  $U = 1590.8(2) \text{ Å}^3$ ;  $\rho_{\text{calcd}} = 1.455 \text{ Mg m}^{-3}$ ;  $2\theta_{\text{max}} = 56.74^\circ$ ; Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ Å}$ );  $\phi-\omega$ -scans; 27 111 reflections collected, 7394 unique (all included in refinement); correction for Lorentzian polarization and absorption: Semi-empirical from equivalents (program SADABS;<sup>17</sup>  $\mu = 0.559 \text{ mm}^{-1}$ , max. and min. transmission 0.6633 and 0.5489); solution: direct methods ((SHELXS-97<sup>17</sup>); refinement: Full-matrix least-squares against  $|F^2|$  (SHELXL-97-2<sup>17</sup>), 521 parameters; hydrogen atoms of methyl groups were added at calculated positions and refined using a riding model, all other hydrogen atoms were located in the difference Fourier map and allowed to refine freely;  $R_1 = 0.043$ ,  $wR_2 = 0.108$  (all data); max/min residual electron density:  $0.40/-0.45 \text{ e}^-/\text{Å}^3$ ; deposited at the Cambridge Crystallographic Data Centre, no. CCDC 718586. Crystal data for **3** (293(2) K):  $0.50 \times 0.4 \times 0.1 \text{ mm}^3$ ; triclinic;  $P\bar{1}$ ;  $a = 10.3495(1)$ ,  $b = 10.6187(1)$ ,  $c = 17.4583(2) \text{ Å}$ ,  $\alpha = 100.014(2)^\circ$ ,  $\beta = 96.329(2)^\circ$ ,  $\gamma = 115.590(2)^\circ$ ,  $U = 1666.0(3) \text{ Å}^3$ ;  $\rho_{\text{calcd}} = 1.572 \text{ Mg m}^{-3}$ ;  $2\theta_{\text{max}} = 53.38^\circ$ ; Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ Å}$ );  $\phi-\omega$ -scans; 12 358 reflections collected, 6193 unique (all included in refinement); correction for Lorentzian polarization and absorption: Semi-empirical from equivalents (program SADABS;<sup>17</sup>  $\mu = 0.850 \text{ mm}^{-1}$ , max. and min. transmission 0.9198 and 0.6763); solution: direct methods (SHELXS-97<sup>17</sup>); refinement: Full-matrix least-squares against  $|F^2|$  (SHELXL-97-2<sup>17</sup>), 442 parameters; hydrogen atoms attached to oxygen were located in the difference Fourier map and allowed to refine freely, all other hydrogen atoms were added at calculated positions and refined using a riding model;  $R_1 = 0.049$ ,  $wR_2 = 0.114$  (all data); max/min residual electron density:  $0.46/-0.34 \text{ e}^-/\text{Å}^3$ ; deposited at the Cambridge Crystallographic Data Centre, no. CCDC 718585. The quality of the crystals of compound **3** was such that data was only collected to a  $2\theta$  angle of  $49^\circ$ , increasing the effect of the square detector on the final completeness to the highest recorded angle (completeness to  $\theta = 26.69^\circ$  is 87.9%).
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