

An unprecedented co-crystal including a *cis*-high-spin and a *trans*-low-spin Fe^{II} complex molecule

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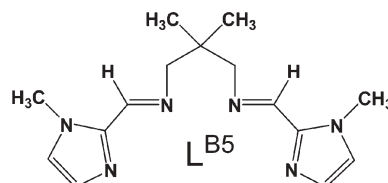
Two structurally and magnetically nonequivalent isomeric molecules, a *cis*-high-spin and a *trans*-low-spin isomer constitute the unit cell of a new iron(II) complex $\{cis-[FeL^{B5}(NCS)_2] \cdot trans-[FeL^{B5}(NCS)_2]\} \cdot CH_3OH$, **1**, ($L^{B5} = N,N'$ -bis((2-*N*-methylimidazol-1-yl)methylene))-2,2-dimethylpropane-1,3-diamine); the synthesis, X-ray structure, and magnetic and Mössbauer study of this unique example of co-crystallised geometric, conformational and electronic isomers are reported.

The co-crystallisation of metal complexes is unusual because compounds with different geometries rarely possess similar lattice packing forces, nor they exhibit similar crystallization kinetics.¹ To date, very few co-crystallised complexes have been reported.^{2–8} These examples show geometrical isomers^{2–5} or different coordination degrees of the ligand.⁶ An example of isomers with different oxidation state has been described recently in the case of a (Cu^I/Cu^{II}) complex.⁷ The system $\{[Ni(PBzPh_2)_2Br_2]\}$ (square planar, diamagnetic), $[Ni(PBzPh_2)_2Br_2]_2$ (tetrahedral, paramagnetic)}, where PBzPh stands for bis(benzylidiphenylphosphine),⁸ is the unique example of both magnetic and stereochemical isomers published to date.

As part of our search for novel spin crossover (SC) materials, we have recently reported on several series of ferrous complexes based on related symmetrical and dissymmetrical tetradentate ligands with an N₄ donor set.^{9–11} Among these ligands, the L^{Bx} series includes symmetrical Schiff bases resulting from the bis-condensation of 2,2-R¹-1,3-diaminopropane (R¹ = Me) with various R²-imidazole-carbaldehydes (R² = 2-H for L^{B1},⁹ 2-Me for L^{B2},⁹ 2-Ph for L^{B3},⁹ 1-(N)H for L^{B4},¹¹ 1-(N)Me for L^{B5}).¹¹ The NCS anions are *trans* to each other, the ligand L^{Bx} is planar and the Fe^{II} centre is high-spin (HS) in all $[FeL^{Bx}(NCS)_2]$ complexes,^{9–11} except $[FeL^{B5}(NCS)_2]$,¹¹ where the NCS anions are *cis* to each other, the ligand L^{Bx} is folded and the Fe^{II} centre is HS. Another peculiarity was that, at variance with all other $[FeL^{Bx}(NCS)_2]$ compounds, $[FeL^{B5}(NCS)_2]$ was obtained systematically (and reproducibly) during the synthesis of $[FeL^{E4}(NCS)_2]$ ($L^{E4} = N$ -[(1-*N*-methylimidazol-2-yl)methylene]-*N'*-(1-pyridin-2-ylethylidene))-2,2-methylpropane-1,3-diamine) as orange-red single crystals, co-crystallised (~11%) with dark blue single crystals of $[FeL^{E4}(NCS)_2]$.¹¹

These peculiarities encouraged us to further explore the reaction between L^{B5} and Fe(NCS)₂·xMeOH:‡ unexpectedly,

this reaction reproducibly yielded the [*cis*-high-spin] and [*trans*-low-spin] isomers co-crystallised as the $\{cis-[FeL^{B5}(NCS)_2] \cdot trans-[FeL^{B5}(NCS)_2]\} \cdot CH_3OH$ compound (**1**) reported in this communication.‡



The most significant characteristic in the structure of **1** is the presence of both *cis* and *trans* isomers of the $[FeL^{B5}(NCS)_2]$ molecule (Fig. 1) in the asymmetric unit. Two five- and one six-membered metallacycles result from coordination of the tetradentate ligand L^{B5}. The interatomic distances of the Fe–N₆ cores allow concluding that the Fe²⁺ cation is in the HS state in the *cis* isomer and low-spin (LS) in the *trans* isomer. Indeed, the average Fe–N bond length for Fe2 (*cis* isomer) is 2.180 Å while it is 1.962 Å for Fe1 (*trans* isomer). The distortion of the Fe–N₆ octahedron as

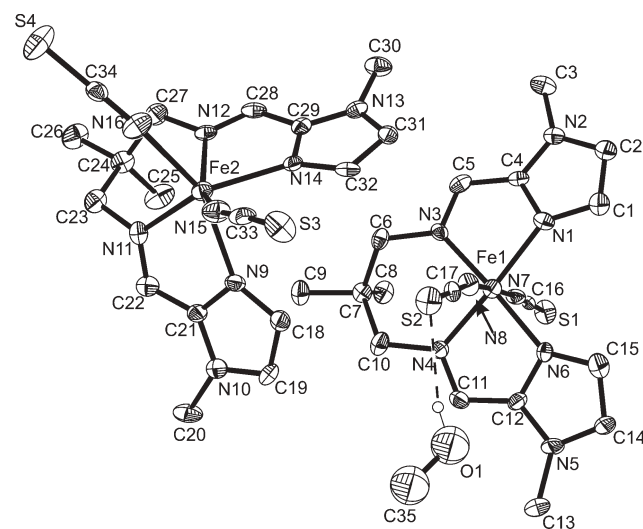


Fig. 1 Labelled ORTEP view of the *cis* and *trans* isomers constituting the asymmetric unit of **1**. Thermal ellipsoids are drawn at the 40% probability level; H-atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe1–N1 2.017(4), Fe1–N3 1.930(4), Fe1–N4 1.945(4), Fe1–N6 1.991(4), Fe1–N7 1.944(4), Fe1–N8 1.945(4), Fe2–N9 2.234(4), Fe2–N11 2.231(4), Fe2–N12 2.257(4), Fe2–N14 2.133(4), Fe2–N15 2.125(5), Fe2–N16 2.098(5); N1–Fe1–N4 174.70(19), N3–Fe1–N6 176.84(19), N7–Fe1–N8 176.74(19), N9–Fe2–N12 114.48(15), N11–Fe2–N14 135.56(16), N15–Fe2–N16 87.06(17).

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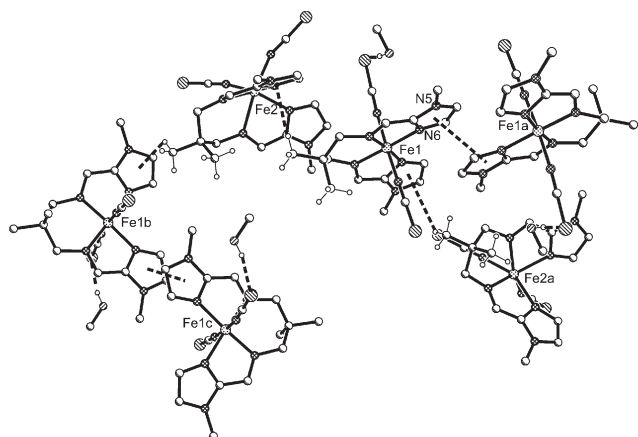


Fig. 2 Perspective view of the crystal packing of **1**.

well as the conformational characteristics of L^{B5} in the two isomers are also clearly different (Fig. 1). For the *trans* isomer, the dihedral angles between the five- and six-membered metallacycles of L^{B5} equal 9.3 and 9.7° whereas L^{B5} is folded in the *cis* isomer, with the corresponding dihedral angles equal to 68.2 and 25.9°, respectively, and with significant elongations of the Fe2–N bonds involving N9, N11 and N12 compared to those with N14, N15 and N16. The asymmetric unit also includes one molecule of methanol disordered over two positions and hydrogen bonded to the sulfur atom S2 of one *trans*-NCS. The ratio between these two positions is 0.40 : 0.60.

The crystal packing may be described as a 3D supramolecular structure (Fig. 2), which is based on a network of π – π stacking and weak C–H \cdots π contacts. The presence of π – π stacking is evidenced by the short centroid-to-centroid distance (3.974(4) Å) between centrosymmetrically related imidazole rings including N5 and N6. Weak C–H \cdots π contacts involve H atoms belonging to the methyl groups (from the 2,2-methylpropane fragment of both *cis* and *trans* isomers and from the 1-*N*-methylimidazolyl fragment of *cis* isomers) and imidazole rings of adjacent *cis* or *trans* complex molecules. These H atoms are almost perfectly centred over the aromatic rings, suggesting that directional weak C–H \cdots π contacts further contribute the supramolecular assembly of complex molecules to yield the crystal. The disordered outer-sphere methanol molecules reside in the cavities formed by the packing of the bulky components of the structure and are H-bonded with sulfur atoms of the coordinated thiocyanate groups. It is noteworthy that, at variance with the 3D supramolecular structure of **1**, the crystal packing of pure *cis*-[FeL^{B5}(NCS)₂] was described as isolated dimeric units stabilized through π – π stacking interactions between centrosymmetrically related [FeL^{B5}(NCS)₂] complex molecules.¹¹

Magnetic studies show that the $\chi_M T$ product of **1** is constant and equal to 1.5 cm³ mol^{−1} K between 80 and 300 K, in agreement with the 1 : 1 ratio of HS and LS Fe^{II} sites evidenced by the crystal structure. Mössbauer spectra have been recorded in the 80–250 K temperature range (Fig. 3); fitting of the spectra evidence one LS (blue) and one HS doublets (red) in a *ca.* 1 : 1 ratio at each temperature (at 80 K, for example, $\delta(\text{LS}) = 0.448(5)$, $\Delta E_Q(\text{LS}) = 0.788(9)$, $\Gamma_{1/2}(\text{LS}) = 0.146(6)$; $\delta(\text{HS}) = 1.111(5)$, $\Delta E_Q(\text{HS}) = 2.687(9)$, $\Gamma_{1/2}(\text{HS}) = 0.131(7)$ mm s^{−1}; $x(\text{HS}) = 0.48(2)$).

In conclusion, {*cis*-[FeL^{B5}(NCS)₂]}·*trans*-[FeL^{B5}(NCS)₂]}·CH₃OH, **1**, is among the rare examples of co-crystallisation of two

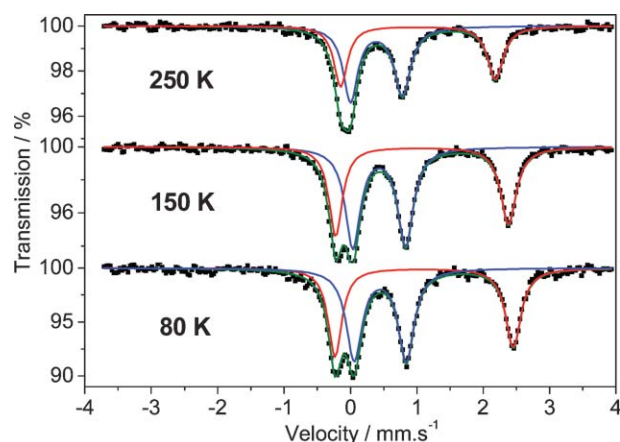


Fig. 3 Selected Mössbauer spectra of **1**. The solid lines represent the fitted spectra (blue: LS site, red: HS site).

isomers: in this unique case, the HS *cis*-[FeL^{B5}(NCS)₂] and the LS *trans*-[FeL^{B5}(NCS)₂] molecules are the components of the unit cell; this implies that the difference of stability between the two isomers is so small that they coexist as complementary components cooperating to the building of the elementary unit of the crystal. This cooperative process may be attributed to the simultaneous effect of steric interactions between the methyl groups of the imidazole moieties and weak C–H \cdots π contacts that occur either between HS *cis*-[FeL^{B5}(NCS)₂] and LS *trans*-[FeL^{B5}(NCS)₂] molecules, or among *cis*-[FeL^{B5}(NCS)₂] molecules. Some time ago, it has been suggested⁸ to name “interallogons” stereochemical isomers constituting the unit cell of a crystal; in other words, “interallogons” are the building units required for the co-crystallisation process. In the case of complex **1**, the “interallogons” are simultaneously magnetic isomers. In addition, strikingly the *trans*-[FeL^{B5}(NCS)₂] molecule is associated with the LS Fe^{II} state while Fe^{II} is in the HS state for all other reported *trans*-[FeL^{Bx}(NCS)₂] molecules.^{9–11} The formation of {*cis*-[FeL^{B5}(NCS)₂]}·*trans*-[FeL^{B5}(NCS)₂]}·CH₃OH, **1**, and its unprecedented characteristics may originate from the presence of 1-*N*-methylimidazole termini in L^{B5} which prevent operation of hydrogen bonds, at variance with parent [FeL^{Bx}(NCS)₂] molecules.^{9–11} Finally, it is remarkable that formation of the isolated HS *cis*-[FeL^{B5}(NCS)₂] molecule was reproducibly obtained as the minor product during the synthesis of [FeL^{E4}(NCS)₂], L^{E4} = *N*-[(1-*N*-methylimidazol-2-yl)methylene]-*N'*-(1-pyridin-2-ylethylidene)-2,2-methylpropane-1,3-diamine being a dissymmetrical tetradentate ligand including the 1-*N*-methylimidazole fragment.¹⁰ This direct reaction, when carried out precisely as described in the footnote† yields {*cis*-[FeL^{B5}(NCS)₂]}·*trans*-[FeL^{B5}(NCS)₂]}·CH₃OH, **1**, characterised by the presence of both HS *cis*-[FeL^{B5}(NCS)₂] and LS *trans*-[FeL^{B5}(NCS)₂] isomers conformers in the unit cell.

Notes and references

† The ligand L^{B5} was prepared as previously described.¹¹ one equivalent of 2,2-dimethyl-1,3-diaminopropane (0.204 g, 2.10^{−3} mol) and two equivalents of 1-*N*-methylimidazole-2-carbaldehyde (0.440 g, 4.10^{−3} mol) were mixed into 20 mL of methanol and stirred for 2 h at room temperature. Slow evaporation of the solvent yielded a pale yellow oil characterized by

^1H NMR (0.468 g, 82%). $\text{Fe}(\text{NCS})_2 \cdot x\text{MeOH}$ was synthesized in a glove-box through the 1 : 2 reaction between $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ with potassium thiocyanate in MeOH (10 mL). After removal of potassium perchlorate through filtration, the freshly prepared $[\text{Fe}(\text{NCS})_2] \cdot x\text{MeOH}$ (10^{-3} mol) was slowly added under stirring to (0.286 g, 10^{-3} mol) of L^{B5} in methanol (10 mL). The colour of the solution turned immediately from pale yellow to deep orange. The stirring was maintained for 30 min, and then stopped. Slow evaporation of the reaction mixture allowed to isolate orange single crystals of $\{\text{cis-}[\text{FeL}^{\text{B5}}(\text{NCS})_2]\text{-trans-}[\text{FeL}^{\text{B5}}(\text{NCS})_2]\} \cdot \text{CH}_3\text{OH}$, **1**, suitable for X-ray measurements (0.32 g, 81%). Elemental analysis: Calc./found (%) for $\text{Fe}_2\text{C}_{35}\text{H}_{48}\text{N}_{16}\text{S}_4\text{O}$ ($M = 949 \text{ g mol}^{-1}$): C, 44.31/44.13; H, 5.10/4.85; N, 23.62/23.35; S, 13.52/13.21; Fe, 11.77/11.44.

‡ Crystal data for $\{\text{cis-}[\text{FeL}^{\text{B5}}(\text{NCS})_2]\text{-trans-}[\text{FeL}^{\text{B5}}(\text{NCS})_2]\} \cdot \text{CH}_3\text{OH}$: $\text{Fe}_2\text{C}_{35}\text{H}_{48}\text{N}_{16}\text{S}_4\text{O}$; $T = 180 \text{ K}$; $M = 948.83$, monoclinic, space group $P2_1/c$, $a = 9.3641(13)$, $b = 17.591(2)$, $c = 28.103(3) \text{ \AA}$, $\beta = 108.408(10)^\circ$, $V = 4390.5(9) \text{ \AA}^3$, $Z = 4$, $D_c = 1.435 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.901 \text{ mm}^{-1}$, 29236 reflections measured, 7755 unique ($R_{\text{int}} = 0.1117$); $R = 0.0591$, $wR = 0.0672$, $\Delta\rho_{\text{max, min}} = 0.456, -0.322 \text{ e \AA}^{-3}$, GOF = 0.908. CCDC 653553. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710734j

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