metal-organic compounds

Co-crystallized *cis* and *trans* isomers of dichlorobis(2-picolylamine)iron(II)

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The octahedral *cis* and *trans* isomers of dichlorobis(2-picolylamine)iron(II), $[FeCl_2(C_6H_8N_2)_2]$, co-crystallize in a 1:1 ratio. The *cis* isomer lies on a twofold axis, whereas the *trans* isomer lies on an inversion centre. The structure is fully ordered, with both Fe atoms in a pure high-spin state. The Fe, Cl and $N(H_2)$ atoms of both isomers lie in the same plane, allowing all Cl and amine H atoms to be engaged in extensive two-dimensional hydrogen bonding. The hydrogen-bonded layers are interconnected through π–π interactions between the pyridine rings. Searches in the Cambridge Structural Database uncover very few examples of such isomer co-existence.

Comment

Preparation of the methanol, ethanol, 1-propanol, 2-propanol, *tert*-butanol and allyl alcohol solvates of tris(2-picolylamine)-iron(II) dichloride from the corresponding alcohol solutions is straightforward (Hostettler *et al.*, 2004). An attempt to synthesize the 1-butanol solvate, however, resulted in co-crystals of the *cis* and *trans* isomers of the title compound, (I), dichlorobis(2-picolylamine)iron(II) (Fig. 1).

cis-(I)   *trans*-(I)
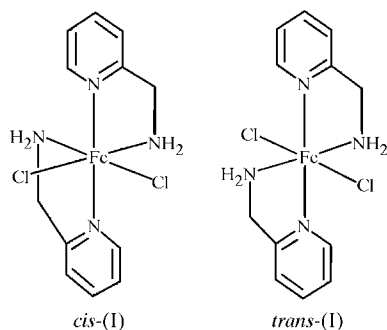
The *cis*-configured molecule has a twofold symmetry axis, while the *trans* isomer is located on an inversion centre. The Fe—N bond distances indicate that both Fe atoms are in a high-spin state. Nonetheless, chemically comparable Fe–ligand

bond lengths differ slightly between the two isomers (Table 1). The Fe—NH_2 bonds lengthen by 0.030 (2) Å on going from the *trans* to the *cis* isomer. This change is almost compensated for by a corresponding decrease of the Fe—Cl bond length by 0.033 (1) Å. A larger difference of 0.045 (2) Å is found for the Fe—N(py) bonds, with the distances in the *cis* isomer being longer.

The only other FeN_4L_2 compounds for which at least an approximate comparison can be made are *trans*-diisothiocyanatobis[4-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole]iron(II) and *cis*-diisothiocyanatobis[3-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole]iron(II) [Cambridge Structural Database (CSD; Allen, 2002) refcodes FADVUC and FADWAJ (Zhu *et al.*, 2002)]. In this case, the *trans* and *cis* isomers actually differ in the substitution of the peripheral benzene rings, but the variation in the coordination geometry shows an effect similar to that observed in (I), the Fe—NCS distances in the *trans* isomer being longer by 0.063 (3) Å than those in the *cis* isomer. This difference is compensated for by a decrease in the Fe—N(triazole) bond length of 0.056 (3) Å. In contrast with (I), the Fe—N(py) distances are almost the same in these two isomers. The structural *cis/trans* influence has been studied in detail elsewhere (Pidcock *et al.*, 1966; Coe & Glenwright, 2000; Gupta *et al.*, 2000).

In the *trans* isomer of (I), symmetry dictates an N(py)—Fe—N(py) angle of 180°, but in the *cis* form the corresponding angle is smaller by about 17°. The dihedral angles between the two pyridine rings are 0 and 72.9 (1)° in the *trans* and *cis* isomers, respectively, and 50° on average in the tris(picolylamine)iron(II) series of solvates (Hostettler *et al.*, 2004). The trend in conformational angles correlates with the observed lengthening of the Fe—N(py) distances from the *trans* to the *cis* isomer of (I) (Table 1), while the average Fe—N(py) *trans* distance in the high-spin tris(picolylamine)iron(II) complexes is intermediate, at 2.21 Å (Chernyshov *et al.*, 2003; Hostettler *et al.*, 2004).

The crystal structure of (I) may be considered as being built from layers of *cis* isomers alternating with layers of *trans* isomers along the (100) direction. Alternatively, the structure may be viewed in terms of layers parallel to the (10$\bar{1}$) planes. In these layers, *cis* and *trans* isomers are connected through N—H···Cl hydrogen bonds, which form a two-dimensional network of 'tiles' in the shape of eight-membered rings, four
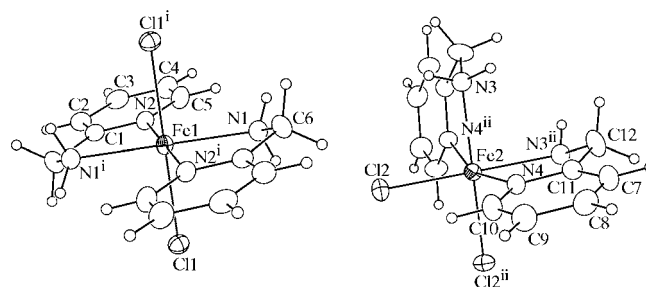

Figure 1
The *trans* (left) and *cis* (right) isomers of (I). Atom Fe1 sits on an inversion centre and atom Fe2 on a twofold axis. Anisotropic displacement parameters are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2} - x$, $\frac{3}{2} - y$, $-z$; (ii) $1 - x$, y, $\frac{1}{2} - z$.]

around each Fe atom (Fig. 2). The hydrogen-bonded layers are stacked through π–π interactions, with typical centroid-to-centroid distances of 3.619 (1) Å (Fig. 3 and Table 2).

As discussed in the *Experimental* section, searches in the CSD (Version 5.25, November 2003 update with 298 097 entries) for other co-crystals of *cis*- and *trans*-MN_4L_2 complexes have revealed only one other example with an ordered crystal structure, namely dichlorobis(2-methyl-1,3-propanediamine)cobalt(III) chloride methanol solvate. The *trans* isomer is located on an inversion centre, whereas the *cis* isomer lies in a general position [CSD refcode CAWPOF (Mather *et al.*, 1983); M is any transition metal ion, N is any type of nitrogen ligand, and L is a halogen, O, S, N or P atom].

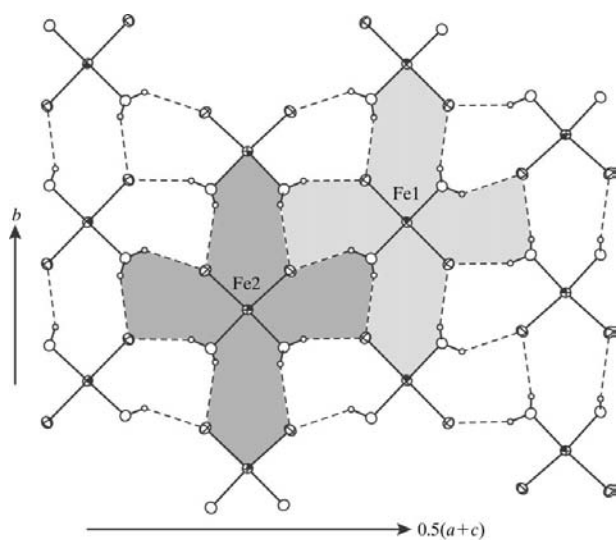The rare occurrence of the *cis/trans* co-crystallization phenomenon may be understood intuitively. Firstly, the two isomers are expected to have different energies and also, most probably, different synthesis conditions, and are therefore not necessarily present simultaneously during synthesis and subsequent crystallization. Secondly, co-crystallization must be more favourable in thermodynamic and/or kinetic terms than crystallization of the individual isomers.
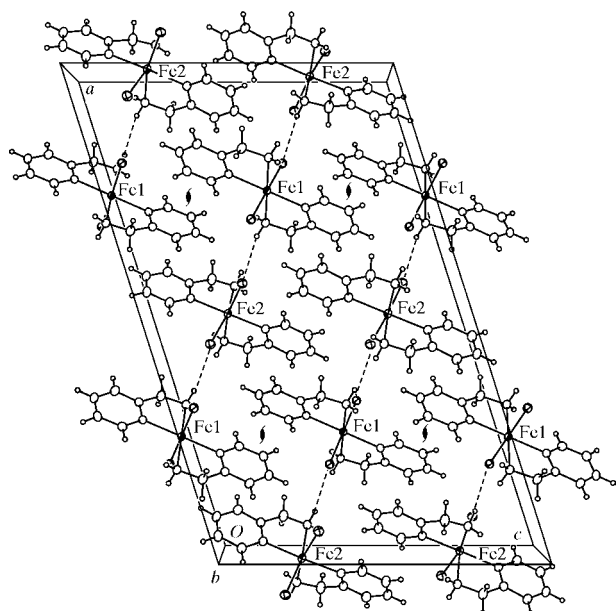
Experimental

A mixture of 2-picolylamine (1-pyridin-2-ylmethanamine; 2.4 mmol) and $FeCl_2\cdot4H_2O$ (0.7 mmol) in 1-butanol (120 ml) was left standing with partial reflux under an N_2 atmosphere at $\sim$355 K for 5 d. A minute quantity of yellow crystals was found in the round-bottomed flask just below the surface of the reaction liquid, and these were shown to contain a 1:1 *cis* and *trans* mixture of (I). Exposed to the air, the crystals deteriorate within hours.

The search in the CSD for MN_4L_2 fragments with any transition metal (M) coordinated to four N atoms and to any two other atoms (L), with M–ligand bond type 'ANY', resulted in 11 769 hits, while a search for crystal structures with $Z' \geq 2$ with reported coordinates resulted in 21 665 hits. Combining the two sets led to 605 hits. Only two of these show both the *cis* and *trans* isomers in the unit cell, namely refcodes CAWPOF (Mather *et al.*, 1983), discussed in the *Comment*, and UCAHUB (Kozmin *et al.*, 2001), *viz.* (propylene-1,2-diamine-*N,N'*)dichlorodinitroplatinum(IV). The latter is disordered, and both sites in the asymmetric part of the unit cell have been modelled with a superposition of *cis* and *trans* isomers. Therefore, this crystal structure cannot be considered an unambiguous case of *cis/trans* co-crystallization.

The CSD was also searched for $Fe^{II}N_4L_2$ complexes for which the *cis* and *trans* isomers are found in different crystals (L is any non-cyclic ligand atom). Among these 338 crystal structures, there are three pairs of *cis* and *trans* isomers. RUHLUB and RUHMAI (Guilard *et al.*, 1997) refer to the respective *trans* and *cis* isomers of the complex dichloro(1,4,8,11-tetraazacyclotetradecane)-iron(III). These were obtained in the same synthesis, but the *trans* isomer crystallizes with a tetrachloroiron(III) anion, while the *cis* isomer has a chloride counter-ion. FEVKAS and FEVMIC (Meyer *et al.*, 1999) refer to the respective *trans* and *cis* isomers of the complex diazido(1,4,8,11-tetraazacyclotetradecane)iron(III). The *trans* isomer crystallizes with a hexafluorophosphate and the *cis* isomer with a perchlorate anion. Both compounds were obtained from the same reaction mixture but at different temperatures, *viz.* 323 and 291 K, respectively. FADVUC and FADWAJ (Zhu *et al.*, 2002), discussed in the *Comment*, refer to compounds with the same chemical sum formulae, with *trans*- and *cis*-coordination geometry, but with ligands differing in the position of the methyl group on the benzene rings. Finally, we are aware of the analogous example of dithiocyanatobis[4-*p*(or *m*)-methylphenyl-3,5-bis(pyridin-2-yl)-1,2,4-triazole]iron(II), which displays a $Cd^{II}O_4L_2$ coordination geometry (Soldatov *et al.*, 2001).

Figure 2
The chessboard layer of hydrogen-bonded complexes, viewed in the ($\bar{1}01$) plane.

Figure 3
The structure of (I), viewed along the *b* axis.

Data collection

Siemens SMART 1K CCD area-detector diffractometer	2676 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 28.1°$
	$h = -33 \rightarrow 34$
$T_{min} = 0.671$, $T_{max} = 0.775$	$k = -8 \rightarrow 8$
14985 measured reflections	$l = -22 \rightarrow 21$
3276 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 2.1803P]$
$wR(F^2) = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
3276 reflections	$\Delta\rho_{max} = 0.39$ e Å⁻³
174 parameters	$\Delta\rho_{min} = -0.23$ e Å⁻³
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Fe1—N1	2.1969 (14)	Fe2—N4	2.2198 (14)
Fe1—N2	2.1746 (13)	Fe1—Cl1	2.4939 (4)
Fe2—N3	2.2267 (14)	Fe2—Cl2	2.4613 (5)
N1—Fe1—N1ⁱ	180.00 (7)	N3—Fe2—N3ⁱⁱ	87.58 (8)
N1—Fe1—Cl1	91.35 (4)	N3—Fe2—Cl2ⁱⁱ	167.06 (4)
N1ⁱ—Fe1—Cl1	88.65 (4)	N3—Fe2—Cl2	89.77 (4)
N2—Fe1—N1	102.87 (5)	N4—Fe2—N3	91.94 (5)
N2ⁱ—Fe1—N1	77.13 (5)	N4—Fe2—N3ⁱⁱ	75.68 (5)
N2—Fe1—Cl1	89.57 (4)	N4ⁱⁱ—Fe2—N4	162.99 (8)
N2ⁱ—Fe1—Cl1	90.43 (4)	N4—Fe2—Cl2ⁱⁱ	99.68 (4)
N2—Fe1—N2ⁱ	180.00 (6)	N4—Fe2—Cl2	91.76 (4)
Cl1—Fe1—Cl1ⁱ	180.00 (2)	Cl2ⁱⁱ—Fe2—Cl2	95.51 (2)

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (ii) $-x + 1, y, -z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl2	0.92	2.70	3.4358 (15)	137
N1—H1B···Cl1ⁱⁱⁱ	0.92	2.68	3.4440 (15)	141
N3—H3A···Cl1ⁱⁱⁱ	0.92	2.62	3.4762 (15)	156
N3—H3B···Cl2ⁱⁱⁱ	0.92	2.81	3.4678 (15)	129

Symmetry code: (iii) $x, y - 1, z$.

H atoms were located geometrically and treated as riding, with C—H distances in the range 0.95–0.99 Å and N—H distances of 0.92 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *PLATON* (Spek, 2003).

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