

Structure of Tris(2-picolyamine)zinc(II) Dichloride–Ethanol, $[\text{Zn}(\alpha\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$; a Complex Related to an Fe^{II} Spin Crossover Complex*

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(Received 16 December 1980; accepted 27 July 1981)

Abstract

The crystal structure of $[\text{Zn}(\alpha\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, $[\text{Zn}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_6\text{O}$, was determined by X-ray diffraction. The space group is $P2_1/c$, with $Z = 4$, $a = 11.906(3)$, $b = 21.929(2)$, $c = 11.557(2)$ Å, $\beta = 124.65(2)^\circ$ and $U = 2482.1(9)$ Å³. The structure was solved by the heavy-atom method and refined by full-matrix least squares to $R = 0.052$ for 3862 independent reflections. The zinc complex is isostructural with the analogous Fe^{II} spin crossover complex, $[\text{Fe}(\alpha\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, in its high-spin state. The average Zn–N bond length of 2.179(5) Å is closer to the high-spin Fe–N bond length 2.195(5) Å than to the low-spin Fe–N distance of 2.013(2) Å. The solvate ethanol molecule exhibits similar orientational disorder to that observed in the high-spin Fe^{II} structure. All the amino N atoms of the complex and the ethanol molecules are hydrogen bonded to Cl^- anions forming a two-dimensional network parallel to the (100) plane.

Introduction

The diimine spin crossover complexes of Fe^{2+} have been studied from different aspects, such as magnetic properties, vibration modes, thermodynamical changes and crystal structures, as the drastic changes in the two spin states bring about many interesting phenomena. We determined the crystal structures of $[\text{Fe}(\alpha\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ in its high-spin state (298, 150 K) and low-spin state (90 K), and elucidated some pronounced differences between both states (Mikami, Konno & Saito, 1979). Remarkable changes in the Fe–N bond length and orientational disorder of ethanol, only in the high-spin state, were observed. The Fe^{II} complex undergoes a spin phase transition in the temperature range 150–100 K, changing from the

high-spin state ($t_{2g}^4 e_g^2$) to the low-spin state (t_{2g}^6) and magnetically from paramagnetic to diamagnetic. This spin phase transition is known to occur even when the Fe^{II} complex is diluted with the diamagnetic Zn^{II} complex to less than 0.1% (Gütlich, Link & Steinhäuser, 1978; Sorai, Ensling & Gütlich, 1976). It is necessary to clarify the structure of the zinc complex together with that of the iron complex and at the same time to determine the behavior of the solvate ethanol molecule in order to understand the nature of this spin transition mechanism. In this connection, we have recently synthesized the zinc picolyamine complex, $[\text{Zn}(\alpha\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, and determined its crystal structure to gain a deeper insight into the ferrous spin transition mechanism and to investigate the nature of the metal–ligand bond.

Experimental

The synthesis of the title compound was carried out in a dry Ar atmosphere. Zinc(II) chloride was dissolved in deoxygenated ethanol, to which was added an ethanolic solution of 2-picolyamine in a slightly excess stoichiometric amount. The solution became transparent as the reaction, which produced white and red colors upon initial mixing of the solutions, proceeded. When the resulting solution was cooled, $[\text{Zn}(\alpha\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ precipitated as a white powder. Recrystallization from ethanol produced transparent rhomboidal crystals.

Table 1. Crystal data of $[\text{M}^{\text{II}}(\alpha\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$

Monoclinic, space group $P2_1/c$, $Z = 4$			
$M =$	Zn	Fe (high spin)	Fe (low spin)*
a	11.906 (3) Å	11.831 (3) Å	11.616 (3) Å
b	21.929 (2)	22.021 (4)	21.546 (3)
c	11.557 (2)	11.551 (3)	11.353 (3)
β	124.65 (2)°	124.28 (2)°	124.41 (2)°
U	2482.1 (9) Å ³	2485.2 (11) Å ³	2344.2 (8) Å ³
D_c	1.356 Mg m ⁻³	1.329 Mg m ⁻³	1.409 Mg m ⁻³

* At 90 K.

* 2-Picolyamine is (2-pyridylmethyl)amine.

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Table 2. Fractional atomic coordinates for non-hydrogen ($\times 10^4$; for Zn $\times 10^5$) and hydrogen atoms ($\times 10^3$) and isotropic thermal parameters

For non-H atoms the equivalent isotropic values of the anisotropic thermal parameters are given: $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	U_{eq} or U ($\text{\AA}^2 \times 10^3$)
Zn ^{II}	2801 (6)	13373 (3)	22016 (6)	36.2 (3)
Cl(1)	2525 (2)	2731 (1)	1787 (2)	62.7 (8)
Cl(2)	-1339 (1)	4312 (1)	3007 (1)	46.3 (7)
N(1)	1080 (5)	1380 (2)	952 (5)	48 (2)
N(2)	2395 (4)	1016 (2)	3667 (4)	45 (2)
N(3)	866 (4)	2208 (2)	3246 (4)	45 (2)
N(4)	-1482 (4)	1938 (2)	772 (4)	42 (2)
N(5)	-693 (4)	497 (2)	1179 (4)	41 (2)
N(6)	-535 (4)	989 (2)	3391 (4)	43 (2)
C(1)	2210 (6)	951 (3)	1481 (6)	55 (3)
C(2)	3052 (5)	926 (2)	3051 (6)	49 (3)
C(3)	4430 (6)	792 (3)	3823 (8)	68 (4)
C(4)	5156 (6)	764 (3)	5257 (9)	81 (4)
C(5)	4513 (7)	862 (3)	5886 (7)	81 (4)
C(6)	3118 (6)	994 (3)	5067 (6)	60 (3)
C(7)	-324 (6)	2577 (3)	2857 (6)	59 (3)
C(8)	-1514 (5)	2450 (2)	1379 (5)	44 (3)
C(9)	-2620 (6)	2847 (3)	682 (7)	60 (4)
C(10)	-3698 (6)	2714 (3)	-660 (7)	66 (4)
C(11)	-3654 (6)	2196 (3)	-1307 (6)	63 (3)
C(12)	-2537 (6)	1829 (2)	-561 (6)	50 (3)
C(13)	-1753 (6)	313 (3)	1377 (6)	56 (3)
C(14)	-1393 (5)	519 (2)	2793 (5)	43 (3)
C(15)	-1967 (6)	234 (3)	3414 (7)	57 (3)
C(16)	-1632 (8)	438 (3)	4693 (7)	63 (4)
C(17)	-748 (7)	919 (3)	5329 (6)	61 (4)
C(18)	-237 (6)	1185 (3)	4650 (6)	53 (3)
O(a)*	3243 (12)	3905 (6)	3620 (13)	82 (3)
O(b)*	4146 (18)	3925 (8)	3587 (19)	87 (5)
O(c)*	2955 (18)	3769 (8)	3944 (19)	93 (5)
CT(1)*	4502 (12)	3902 (5)	4888 (13)	141 (5)
CT(2a)*	5019 (17)	3385 (8)	5744 (19)	75 (5)
CT(2b)*	4420 (29)	3254 (13)	5446 (31)	91 (8)
CT(2c)*	5380 (29)	3615 (14)	6012 (32)	101 (8)
HN(1)	62 (5)	127 (2)	19 (5)	41 (13)
HN(2)	133 (4)	167 (2)	104 (4)	28 (12)
HN(3)	142 (5)	219 (2)	411 (5)	55 (16)
HN(4)	137 (4)	236 (2)	294 (5)	40 (13)
HN(5)	-21 (4)	25 (2)	139 (4)	23 (11)
HN(6)	-106 (6)	52 (3)	26 (6)	77 (20)
H(1)	185 (6)	66 (3)	118 (7)	86 (21)
H(2)	286 (5)	101 (2)	113 (5)	45 (14)
H(3)	486 (5)	76 (2)	339 (5)	45 (14)
H(4)	609 (5)	66 (2)	571 (5)	56 (17)
H(5)	478 (5)	83 (3)	667 (6)	64 (18)
H(6)	263 (5)	105 (2)	540 (5)	42 (14)
H(7)	-66 (4)	245 (2)	343 (5)	43 (14)
H(8)	0 (7)	296 (3)	305 (7)	96 (23)
H(9)	-256 (5)	315 (2)	116 (5)	48 (15)
H(10)	534 (7)	297 (3)	-120 (7)	104 (24)
H(11)	-440 (6)	206 (3)	-227 (7)	80 (20)
H(12)	-247 (6)	148 (3)	-86 (6)	77 (19)
H(13)	-265 (6)	49 (3)	62 (6)	76 (19)
H(14)	-173 (6)	8 (3)	144 (7)	91 (22)
H(15)	-271 (6)	-8 (3)	281 (6)	75 (20)
H(16)	-205 (6)	35 (3)	511 (6)	70 (16)
H(17)	-53 (6)	108 (3)	620 (6)	66 (18)
H(18)	31 (5)	145 (2)	493 (5)	43 (14)

* Population parameters: O(a) 0.41 (4), O(b) 0.29 (1), O(c) 0.30 (3), CT(1) 1.0, CT(2a) 0.41 (4), CT(2b) 0.29 (1), CT(2c) 0.30 (3).

Upon exposure to moist room air the crystals became translucent. For the intensity measurement a single crystal sealed in a Lindemann-glass capillary was used. The general features of the X-ray diffraction patterns indicated that the zinc and iron complexes are isostructural. The reflection data were collected on an automated four-circle diffractometer using Mo $K\alpha$ ($\lambda = 0.7107 \text{ \AA}$) radiation within the range of $2\theta < 55^\circ$, the ω - 2θ scan technique being employed. Crystal data are shown in Table 1.

The structure was solved by the conventional heavy-atom method based on 3862 independent reflections with $|F_o| > 3\sigma(|F|)$. The structure factor calculation based on the atomic coordinates of Zn and Cl gave an R index of 0.45. The atomic parameters were refined by using the least-squares program *RADIEL* (Yang, Becker & Coppens, 1978, unpublished) based on F and using equal weights. Successive Fourier syntheses revealed all the C, N and O atoms of both the complex and the ethanol molecule. The final R value was 0.052. The final positional parameters are listed in Table 2. In the last cycle of the refinement, all the parameter shifts were less than one sixth of the corresponding standard deviations. Atomic scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974) and those for H atoms from Stewart, Davidson & Simpson (1965). Anisotropic thermal parameters were used for all the atoms except H and the disordered C and O atoms.*

Description of the structure and discussion

The present zinc picolylamine complex (Fig. 1) is isostructural with the Fe^{II} analogue, and its molecular geometry is very similar to that of the Fe^{II} complex in its high-spin state. The complex adopts a *mer* con-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36330 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

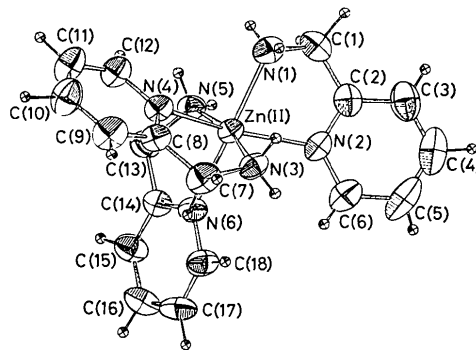


Fig. 1. ORTEP drawing (Johnson, 1965) of the $[\text{Zn}(\alpha\text{-pic})_3]^{2+}$ cation with thermal ellipsoids at 50% probability together with the numbering scheme.

Table 3. Equations of least-squares planes (X , Y and Z in Å) and deviations of atoms from the planes through the six atoms of the pyridine rings

The atoms with asterisks were included in the calculations of the least-squares planes.

Ligand I: $-0.2068X - 0.9767Y - 0.0573Z + 2.4780 = 0.0$

Ligand II: $-0.7852X - 0.5106Y + 0.3504Z + 0.1498 = 0.0$

Ligand III: $0.6201X - 0.6335Y + 0.4628Z + 1.6616 = 0.0$

Ligand I		Ligand II		Ligand III	
N(2)*	0.010 (6)	N(4)*	0.020 (11)	N(6)*	0.003 (8)
C(2)*	-0.009 (7)	C(8)*	-0.007 (12)	C(14)*	0.003 (10)
C(3)*	0.003 (7)	C(9)*	-0.010 (13)	C(15)*	-0.005 (8)
C(4)*	0.001 (7)	C(10)*	0.008 (13)	C(16)*	0.001 (9)
C(5)*	0.001 (8)	C(11)*	-0.003 (12)	C(17)*	0.005 (9)
C(6)*	-0.006 (8)	C(12)*	-0.003 (12)	C(18)*	-0.008 (10)
Zn	-0.276 (4)	Zn	0.260 (9)	Zn	0.082 (7)
N(1)	-0.667 (6)	N(3)	-0.377 (11)	N(5)	0.497 (5)
C(1)	0.018 (7)	C(7)	-0.008 (12)	C(13)	-0.022 (6)

figuration and has no threefold symmetry. The pyridine rings are planar but are not coplanar with the five-membered chelate rings, which are puckered. The equations of the least-squares planes for the pyridine rings and the atomic shifts therefrom are listed in Table 3. The deviations of the amino N atoms from the mean planes are in the range 0.38–0.67 Å.

The bond lengths and angles of the zinc picolylamine complex are given in Tables 4 and 5. The average Zn–N bond length is 2.179 (5) Å, which is much closer to the Fe^{II} high-spin value of 2.195 (5) Å than the low-spin value, 2.013 (3) Å. The average ionic radii for Zn²⁺ and octahedral high-spin Fe²⁺ are reported to be 0.89 and 0.91 Å, respectively (Shannon & Prewitt, 1969). The Zn–N bond lengths for the amino N atoms and pyridine N atoms are significantly different, as was found in the Fe^{II} high-spin-state complex. However, the average bond length of Zn–N_{amine} is 2.143 (5) Å, somewhat shorter than the high-spin Fe–N_{amine} of 2.180 (5) Å, while the Zn–N_{pyr} distance is 2.215 (5) Å, slightly longer than Fe–N_{pyr} of 2.209 Å. The different bond nature of M–N_{amine} and M–N_{pyr} (M = Fe, Zn) is more apparent in the zinc complex than the analogous ferrous complex. The electron configuration of the Zn²⁺ complex is a filled non-bonding d^{10} core which has a small availability of $d\pi$ electrons, resulting in the weaker M–N_{pyr} interaction. On the other hand, the higher electron affinities of Zn²⁺ are associated with greater polarizing power (Dwyer & Mellor, 1964). For the Zn–N_{amine} bond, the contribution of 4s and 4p orbitals of Zn²⁺ increases, which may well be expected to increase the σ bond order with respect to the 3d orbitals. The chelate bite angle, N–Zn–N, is 76.4° on average which agrees well with the value of 75.4° for N–Fe–N in the high-spin state. The mean N...N non-bonded interatomic distance in a ligand is 2.695 (7) Å, slightly longer than that in the Fe^{II} complex. The average bond lengths over three nearly equivalent ligands, apart from a small deviation owing to the *trans* effects (Mikami,

Table 4. Bond distances (Å) with *e.s.d.*'s in parentheses

Zn–N(1)	2.137 (5)	Zn–N(2)	2.204 (5)
Zn–N(3)	2.153 (5)	Zn–N(4)	2.219 (5)
Zn–N(5)	2.139 (5)	Zn–N(6)	2.221 (5)
N(1)–N(2)	2.711 (7)	N(2)–N(6)	3.318 (7)
N(3)–N(4)	2.693 (7)	N(2)–N(3)	3.062 (7)
N(5)–N(6)	2.680 (7)	N(1)–N(5)	2.985 (7)
N(1)–N(3)	3.340 (7)	N(4)–N(6)	3.300 (7)
N(1)–N(4)	3.181 (7)	N(4)–N(5)	3.254 (7)
N(2)–N(5)	3.326 (7)	N(3)–N(6)	3.207 (7)
Ligand I			
N(1)–C(1)	1.462 (9)	Ligand II	
N(2)–C(2)	1.337 (9)	N(3)–C(7)	1.463 (9)
C(1)–C(2)	1.494 (10)	N(4)–C(8)	1.334 (8)
C(2)–C(3)	1.383 (11)	C(7)–C(8)	1.500 (10)
C(3)–C(4)	1.367 (13)	C(8)–C(9)	1.392 (10)
C(4)–C(5)	1.340 (13)	C(9)–C(10)	1.368 (11)
C(5)–C(6)	1.397 (11)	C(10)–C(11)	1.379 (11)
C(6)–N(2)	1.333 (9)	C(11)–C(12)	1.362 (10)
Ligand III			
N(5)–C(13)	1.461 (9)	C(12)–N(4)	1.345 (8)
N(6)–C(14)	1.334 (8)	C(15)–C(16)	1.368 (11)
C(13)–C(14)	1.506 (9)	C(16)–C(17)	1.373 (11)
C(14)–C(15)	1.390 (10)	C(17)–C(18)	1.367 (11)
		C(18)–N(6)	1.356 (9)

Table 5. Bond angles (°) with *e.s.d.*'s in parentheses

N(1)–Zn–N(2)	77.3 (2)	N(5)–Zn–N(6)	75.8 (2)
N(3)–Zn–N(4)	76.0 (2)		
Ligand I			
Zn–N(1)–C(1)	110.3 (5)	Ligand II	
Zn–N(2)–C(2)	113.4 (5)	Zn–N(3)–C(7)	111.7 (4)
N(1)–C(1)–C(2)	110.7 (6)	Zn–N(4)–C(8)	113.9 (4)
C(1)–C(2)–N(2)	116.7 (6)	N(3)–C(7)–C(8)	111.6 (6)
N(2)–C(2)–C(3)	121.8 (7)	C(7)–C(8)–N(4)	117.7 (6)
C(2)–C(3)–C(4)	119.5 (8)	N(4)–C(8)–C(9)	121.5 (6)
C(3)–C(4)–C(5)	119.2 (9)	C(8)–C(9)–C(10)	119.5 (7)
C(4)–C(5)–C(6)	119.5 (8)	C(9)–C(10)–C(11)	119.3 (7)
C(5)–C(6)–N(2)	121.9 (7)	C(10)–C(11)–C(12)	118.0 (7)
C(6)–N(2)–C(2)	118.1 (6)	C(11)–C(12)–N(4)	124.0 (6)
Ligand III			
Zn–N(5)–C(13)	113.4 (5)	C(12)–N(4)–C(8)	117.7 (5)
Zn–N(6)–C(14)	114.9 (5)	C(14)–C(15)–C(16)	119.0 (7)
N(5)–C(13)–C(14)	110.4 (6)	C(15)–C(16)–C(17)	119.6 (7)
C(13)–C(14)–N(6)	117.1 (6)	C(16)–C(17)–C(18)	118.4 (7)
N(6)–C(14)–C(15)	122.4 (6)	C(17)–C(18)–N(6)	123.4 (7)
		C(18)–N(6)–C(14)	117.2 (6)

Table 6. The average bond lengths of *mer*-[M^{II}(pic)₃]Cl₂·EtOH (M = Zn, Fe) (Å)

	High-spin state			Low-spin state
	Zn (298 K)	Fe (298 K)	Fe (150 K)	Fe (90 K)
M–N _{amine}	2.143 (5)	2.180 (5)	2.163 (3)	2.024 (4)
M–N _{pyr}	2.215 (5)	2.209 (5)	2.187 (3)	2.002 (4)
N _{amine} –C	1.462 (9)	1.457 (11)	1.466 (5)	1.483 (6)
N _{pyr} –C	1.335 (8)	1.333 (10)	1.343 (5)	1.363 (6)
C–C	1.500 (10)	1.501 (9)	1.512 (4)	1.497 (6)
N _{pyr} –C _p *	1.345 (9)	1.345 (9)	1.352 (5)	1.347 (6)
C _p –C _p	1.373 (11)	1.377 (11)	1.382 (6)	1.385 (6)
N–M–N	76.4 (2)°	75.4 (2)°	75.8 (1)°	81.6 (2)°

* C_p indicates the C atoms in the pyridine rings.

Konno & Saito, 1980), are compared in Table 6 for the Zn^{II} complex and the Fe^{II} complex at three different temperatures.

The packing feature is exactly the same as that observed in the Fe^{II} complex in its high-spin state. The interatomic distances, including hydrogen bonds, are listed in Table 7. All the amino N atoms of the complex are hydrogen bonded to the two Cl^- ions present in the asymmetric unit. The hydrogen bonds form an infinite zigzag chain along **c**. The complexes are also linked by hydrogen bonds in the **b** direction through Cl^- ions forming a two-dimensional network parallel to the (100) plane. The N—H...Cl distances range from 3.254 to 3.441 Å. The ethanol molecule exhibits orientational disorder and apparently occupies three different sites with one common α -carbon atom. The range of hydrogen-bond lengths O—H...Cl is 3.128–3.216 Å. This is also one of the most remarkable features observed in the Fe^{II} complex in its high-spin state. The population ratio of the disordered ethanol is 4:3:3 in the zinc complex which is more uniform when compared to the 3:2:2 ratio for the analogous Fe^{II} complex at 298 K. From the X-ray evidence that no disorder was observed for ethanol in the structure of the low-spin Fe^{II} complex, and that ordering of ethanol was observed (population ratio 8:1:1) at the upper end of the transition temperature of 150 K (Mikami, Konno & Saito, 1979), this disorder of the solvate molecule clearly seems to be related to the nature of the spin phase transition of the $[Fe(\alpha\text{-pic})_3]$ complex. The entropy value ΔS due to ethanol disorder can be estimated from the population ratio of all the sites by $\Delta S = Rx \ln(x)$. In the present zinc picoline complex, the population ratio 4:3:3 gives a ΔS value of 9.0 J $K^{-1} \text{ mol}^{-1}$. In the case of the Fe^{II} complex at 298 K, the population ratio 3:2:2 leads to a ΔS value of 8.9 J $K^{-1} \text{ mol}^{-1}$, while the 8:1:1 ratio at 150 K gives a ΔS

value of 5.3 J $K^{-1} \text{ mol}^{-1}$. Thus, the entropy contribution of ethanol molecules in this picoline-complex series is almost as large as that caused by change of spin configuration, which is $R \ln(2S + 1) = R \ln 5 = 13.4 \text{ J } K^{-1} \text{ mol}^{-1}$ calculated from the multiplicity of the spin quantum number, or by the change in the Fe—N stretching mode (17.4 J $K^{-1} \text{ mol}^{-1}$), the N—Fe—N deformation mode and lattice vibration which seem to be associated with coupling with the phonon system.

The following interesting behavior of the Fe^{II} complex was observed by means of Mössbauer spectroscopy (Sorai, Enslin & Gütlich, 1976; Gütlich, Link & Steinhäuser, 1978). When the Fe^{II} picoline complex is substituted by isomorphous replacement of Fe^{II} by Zn^{II} , it forms a complete series of solid solutions. As the ratio of Fe^{II} ion decreases, the spin phase transition curve, indicating the fraction of the high-spin-state Fe^{II} against temperature, becomes less steep and the transition temperature is shifted to lower temperature ranges. The most striking aspect of this study is that even when the fraction of Fe^{II} is as small as 0.0009, the complete spin transition still takes place. The dilution of the Fe^{II} spin crossover complex by the diamagnetic zinc complex does indeed influence the spin transition but by no means prevents a complete transition from taking place. The fact that the zinc complex has a structure similar to that of the high-spin Fe^{II} complex may explain the shift of the transition temperature to lower temperatures, thus indicating a preference for the high-spin state. When the fraction of the Fe^{II} complex is less than one sixth and much of the neighboring complex is Zn^{II} , which does not change its spin state but remains in the high-spin structure, the cooperative nature of the spin transition is weakened. However, the spin transition would be transmitted through hydrogen bonds, which exist both in the Zn^{II} and Fe^{II} structures, and would probably be completed by interactions with the order-disorder transition of the ethanol molecule.

Table 7. Intermolecular distances (Å) shorter than $\sim 3.7 \text{ \AA}$

Symmetry code			
None	x, y, z	(iii)	$-x, -y, 1-z$
(i)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	(iv)	$1-x, -y, 1-z$
(ii)	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	(v)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$
C(17)...	Cl(2 ⁱ) 3.759 (9)	O(a)...	C(15 ⁱⁱ) 3.50 (1)
C(18)...	Cl(1 ⁱ) 3.652 (7)	O(a)...	C(13 ⁱⁱ) 3.56 (1)
C(6)...	C(16 ⁱⁱⁱ) 3.690 (8)	O(b)...	C(15 ⁱⁱ) 3.67 (1)
C(17)...	C(15 ⁱⁱⁱ) 3.691 (9)	O(c)...	C(13 ⁱⁱ) 3.61 (2)
C(3)...	C(4 ^{iv}) 3.522 (9)	O(c)...	C(1 ⁱⁱ) 3.57 (2)
C(4)...	C(4 ^{iv}) 3.384 (10)	C(5)...	O(b ⁱ) 3.42 (2)
C(6)...	O(b ⁱ) 3.52 (2)		
Hydrogen-bond distances			
N(1)—HN(2)...	Cl(1) 3.282 (5)	O(a)—H...	Cl(1) 3.128 (11)
N(3)—HN(4)...	Cl(1) 3.441 (5)	O(b)—H...	Cl(1) 3.216 (12)
N(3 ^v)—HN(3)...	Cl(1) 3.388 (4)	O(c)—H...	Cl(1) 3.195 (14)
N(1 ⁱ)—HN(1)...	Cl(2) 3.332 (4)		
N(5 ⁱ)—HN(6)...	Cl(2) 3.317 (5)		
N(5 ⁱⁱ)—HN(5)...	Cl(2) 3.301 (3)		

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