Electronic Supplementary Information for manuscript entitled

$2[Mn(acacen)]^+ + 1[Fe(CN)_5NO]^-$ polynuclear heterobimetallic coordination compounds of different dimensionality in the solid state

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Crystallographic section

The following compounds are structurally characterized:

(**2**) $[\{Mn(acacen)H_2O\}_2Fe(CN)_5NO]\cdot C_2H_5OH$

(**3**) $[\{Mn(acacen)H_2O\}_4(Fe(CN)_5NO][Fe(CN)_5NO]\cdot 4CH_3CN$

(**4**) $[\{Mn(acacen)\}_2(C_3H_7OH)\{Fe(CN)_5NO\}]_n$

(**5**) $[\{Mn(acacen)\}_2Fe(CN)_5NO]_n$

acacen = $C_{12}H_{18}N_2O_2$

Table 1S. Crystal data, data collection and structure refinement parameters for **2** – **5**.

Compound	**2**	**3**	**4**	**5**
Empirical formula	$C_{31}H_{46}FeMn_2N_{10}O_8$	$C_{66}H_{92}Fe_2Mn_4N_{24}O_{14}$	$C_{32}H_{44}FeMn_2N_{10}O_6$	$C_{29}H_{36}FeMn_2N_{10}O_5$
Molecular weight	852.51	1777.10	830.50	770.41
Crystal system	monoclinic	tetragonal	monoclinic	tetragonal
Space group	*C*2/*c*	*P*4/*n*	$P2_1$	$P4_3$
a, Å	19.0620(5)	20.6997(4)	9.8861(6)	10.8355(4)
b, Å	14.5264(4)	20.6997(4)	12.6888(6)	10.8355(4)
c, Å	14.3781(3)	9.9205(5)	16.0244(9)	29.115(2)
β, °	92.3120(10)	90	107.5510(10)	90
V, Å^3	3978.09(17)	4250.7(2)	1916.57(18)	3418.4(3)
Z	4	2	2	4
D_{calc}, g/cm^3	1.423	1.388	1.439	1.497
μ, mm^{-1}	1.043	0.979	1.077	1.199
$2\theta_{max}$, °	63.08	59.32	52.78	55.00
Temperature, K	100.0(2)	120.0(2)	150.0(2)	301(2)
Crystal size, mm	0.49×0.41×0.13	0.36×0.28×0.08	0.145×0.080×0.075	0.14×0.14×0.12
Range *h*, *k*, *l*	$-27 \le h \le 27$, $-21 \le k \le 20$, $-13 \le l \le 19$	$-27 \le h \le 21$, $-19 \le k \le 27$, $-13 \le l \le 13$	$-12 \le h \le 12$, $-15 \le k \le 8$, $-20 \le l \le 20$	$-11 \le h \le 14$, $-14 \le k \le 11$, $-37 \le l \le 37$
Reflns measured	18426	28719	12744	26240
Unique reflns	5529	5309	5791	7849
R_{int}	0.0310	0.0196	0.0313	0.0396
Observed ($I > 2\sigma(I)$)	5037	4574	5111	6158
Refined parameters	251	267	473	435
Restraints	0	0	1	1
R_1, wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0696$, $wR_2 = 0.1314$	$R_1 = 0.0290$, $wR_2 = 0.0690$	$R_1 = 0.0290$, $wR_2 = 0.0598$	$R_1 = 0.0360$, $wR_2 = 0.0752$
R_1, wR_2 (all data)	$R_1 = 0.0770$, $wR_2 = 0.1344$	$R_1 = 0.0371$, $wR_2 = 0.0731$	$R_1 = 0.0381$, $wR_2 = 0.0625$	$R_1 = 0.0831$, $wR_2 = 0.0834$
Goodness-of-fit on F^2	1.255	1.080	1.010	0.954
Largest diff. peak, hole (e Å^{-3})	0.888/ -1.609	0.846/ -0.250	0.408/ -0.327	0.340/-0.221

The disorder in 2 and 3. The nitroprusside anion in **2** and **3** (counter anion only) is disordered over two positions so that iron occupies two close positions switching between disordered CN and NO groups. As nitroprusside anion has similar dimensions despite nitrosyl and cyanogroup being in the axial position, crystal packing is not influenced by the nitroprusside flipping. Since the coordinated NO group is shorter than CN and the terminal atoms of nitroprusside CN groups are fixed within the crystal environment, the iron atom is disordered over two very close positions (~0.5 Å) while light atoms of NO and CN groups coincide (in **3**, Fig 1aS) or almost coincide (in **2**, Fig 1bS). Due to the fact that iron ion usually occupies special positions, the effect is averaged by symmetry. Therefore, elongation in the axial direction a.d.p. ellipsoid of iron atom may point to such disorder. The position of disordered Fe was resolved in both structures followed by decreasing residuals R_1 and wR_2. Our attempts to split disordered positions for CN/NO groups succeeded in **2**, and failed in **3**. In **2** they are refined with anisotropic a.d.p. parameters, while in **3** with both coordinates and a.d.p. parameters set equal.

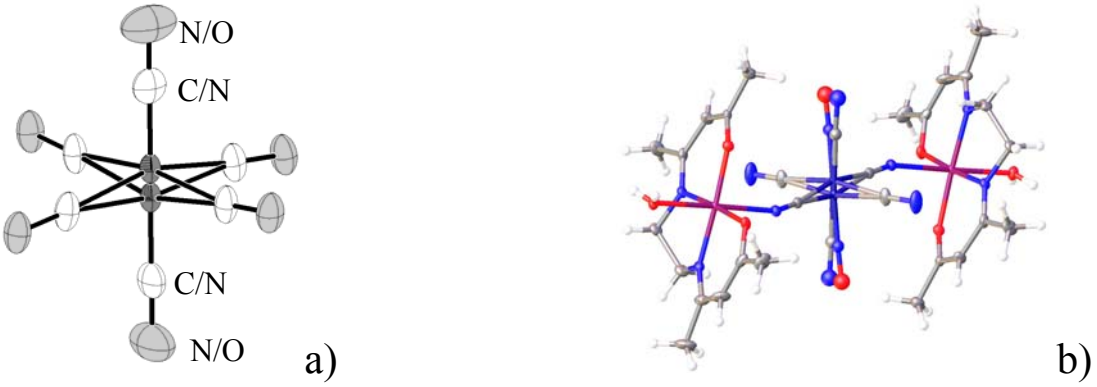

Fig. 1S The disorder model for nitroprusside anions found in **3** (a) and in **2** (b) with mixed and split positions of CN and NO ligands.

Compound 2. $[\{Mn(acacen)H_2O\}_2Fe(CN)_5NO]\cdot C_2H_5OH$

Table 2S. Selected geometric parameters (Å, º) in **2**.

Mn1—O1	1.8970 (10)	C3—C4	1.423 (2)
Mn1—O2	1.9082 (10)	C4—C5	1.510 (2)
Mn1—N2	1.9697 (12)	C6—C7	1.512 (2)
Mn1—N1	1.9710 (13)	C8—C9	1.512 (2)
Mn1—O3	2.2471 (11)	C9—C10	1.431 (2)
Mn1—N13	2.3325 (13)	C10—C11	1.371 (2)
Fe1—N4	1.658 (3)	C11—C12	1.502 (2)
Fe1—C13^{i}	1.9337 (14)	Fe2—Fe2^{iv}	0.5418 (12)
Fe1—C13^{ii}	1.9337 (14)	Fe2—C21	1.532 (3)
Fe1—C13	1.9337 (14)	Fe2—C22	1.9438 (16)
Fe1—C13^{iii}	1.9337 (14)	Fe2—C22^{v}	1.9438 (16)
Fe1—C15	1.945 (3)	Fe2—C22^{iv}	1.9640 (16)
N13—C13	1.1467 (19)	Fe2—C22^{vi}	1.9640 (16)
O4—N4	1.146 (4)	Fe2—C21^{iv}	2.073 (3)
N15—C15	1.147 (4)	Fe2—N21N^{iv}	2.073 (3)
O1—C2	1.2982 (19)	C21—N21	1.154 (4)
O2—C11	1.3036 (18)	C21—Fe2^{iv}	2.073 (3)
N1—C4	1.308 (2)	N22—C22	1.147 (2)
N1—C6	1.4774 (19)	C22—Fe2^{iv}	1.9640 (16)
N2—C9	1.300 (2)	N1S—C1S	1.142 (3)
N2—C7	1.4732 (19)	C1S—C2S	1.454 (4)
C1—C2	1.504 (2)	O3—H31	0.84 (3)
C2—C3	1.372 (2)	O3—H32	0.79 (2)
O1—Mn1—O2	90.58 (4)	C2—C3—C4	126.03 (15)
O1—Mn1—N2	176.26 (5)	N1—C4—C3	122.69 (14)
O2—Mn1—N2	92.63 (5)	N1—C4—C5	120.17 (14)
O1—Mn1—N1	92.60 (5)	C3—C4—C5	117.13 (15)
O2—Mn1—N1	175.13 (5)	N1—C6—C7	108.94 (12)
N2—Mn1—N1	84.33 (5)	N2—C7—C6	108.58 (12)
O1—Mn1—O3	90.39 (4)	N2—C9—C10	122.23 (13)
O2—Mn1—O3	91.31 (4)	N2—C9—C8	121.14 (14)
N2—Mn1—O3	87.62 (5)	C10—C9—C8	116.62 (14)
N1—Mn1—O3	92.36 (5)	C11—C10—C9	125.74 (15)
O1—Mn1—N13	93.49 (4)	O2—C11—C10	125.25 (14)
O2—Mn1—N13	87.44 (4)	O2—C11—C12	114.16 (13)
N2—Mn1—N13	88.57 (5)	C10—C11—C12	120.56 (14)
N1—Mn1—N13	88.68 (5)	Fe2^{iv}—Fe2—C21	180.000 (3)
O3—Mn1—N13	175.93 (5)	Fe2^{iv}—Fe2—C22	84.16 (6)
N4—Fe1—C13^{i}	96.11 (5)	C21—Fe2—C22	95.84 (6)
N4—Fe1—C13^{ii}	96.11 (5)	Fe2^{iv}—Fe2—C22^{v}	84.16 (6)
C13^{i}—Fe1—C13^{ii}	89.352 (10)	C21—Fe2—C22^{v}	95.84 (6)
N4—Fe1—C13	96.11 (5)	C22—Fe2—C22^{v}	168.32 (12)
C13^{i}—Fe1—C13	89.352 (10)	Fe2^{iv}—Fe2—C22^{iv}	79.91 (6)
C13^{ii}—Fe1—C13	167.79 (9)	C21—Fe2—C22^{iv}	100.09 (6)
N4—Fe1—C13^{iii}	96.11 (5)	C22—Fe2—C22^{iv}	88.979 (7)

C13^{i}—Fe1—C13^{iii}	167.79 (9)	C22^{v}—Fe2—C22^{iv}	88.979 (7)
C13^{ii}—Fe1—C13^{iii}	89.352 (10)	Fe2^{iv}—Fe2—C22^{vi}	79.91 (6)
C13—Fe1—C13^{iii}	89.352 (11)	C21—Fe2—C22^{vi}	100.09 (6)
N4—Fe1—C15	180.000 (2)	C22—Fe2—C22^{vi}	88.979 (7)
C13^{i}—Fe1—C15	83.89 (5)	C22^{v}—Fe2—C22^{vi}	88.979 (7)
C13^{ii}—Fe1—C15	83.89 (5)	C22^{iv}—Fe2—C22^{vi}	159.83 (12)
C13—Fe1—C15	83.89 (5)	C21—Fe2—C21^{iv}	180.000 (1)
C13^{iii}—Fe1—C15	83.89 (5)	C22—Fe2—C21^{iv}	84.16 (6)
C13—N13—Mn1	142.86 (11)	C22^{v}—Fe2—C21^{iv}	84.16 (6)
N13—C13—Fe1	175.96 (14)	C22^{iv}—Fe2—C21^{iv}	79.91 (6)
O4—N4—Fe1	180.000 (2)	C22^{vi}—Fe2—C21^{iv}	79.91 (6)
N15—C15—Fe1	180.000 (1)	C21—Fe2—N21N^{iv}	180.000 (1)
C2—O1—Mn1	127.76 (10)	C22—Fe2—N21N^{iv}	84.16 (6)
C11—O2—Mn1	125.95 (9)	C22^{v}—Fe2—N21N^{iv}	84.16 (6)
C4—N1—C6	120.78 (13)	C22^{iv}—Fe2—N21N^{iv}	79.91 (6)
C4—N1—Mn1	125.91 (10)	C22^{vi}—Fe2—N21N^{iv}	79.91 (6)
C6—N1—Mn1	112.57 (10)	N21—C21—Fe2	180.000 (1)
C9—N2—C7	122.08 (12)	N21—C21—Fe2^{iv}	180.000 (1)
C9—N2—Mn1	126.38 (10)	N22—C22—Fe2	167.85 (18)
C7—N2—Mn1	111.25 (10)	N22—C22—Fe2^{iv}	176.18 (18)
O1—C2—C3	124.68 (14)	Fe2—C22—Fe2^{iv}	15.93 (4)
O1—C2—C1	114.46 (14)	N1S—C1S—C2S	178.6 (3)
C3—C2—C1	120.86 (15)	H32—O3—H31	107 (2)

Symmetry code(s): (i) *y*, -*x*+3/2, *z*; (ii) -*x*+3/2, -*y*+3/2, *z*; (iii) -*y*+3/2, *x*, *z*; (iv) *y*+1/2, -*x*+1, -*z*+2; (v) -*x*+3/2, -*y*+1/2, *z*; (vi) -*y*+1, *x*-1/2, -*z*+2.

Hydrogen bonds (Å, º) **in 2.**

Hydrogen bond	D-H	H...A	D...A	<(DHA)	Symmetry operations
O(3)-H(31)...N(41)	0.79(4)	1.99(4)	2.775(4)	172(4)	-x+3/2, y+1/2, -z+1/2
O(3)-H(32)...O(1)	0.75(4)	2.06(4)	2.808(3)	174(4)	-x+3/2, -y+1/2, -z

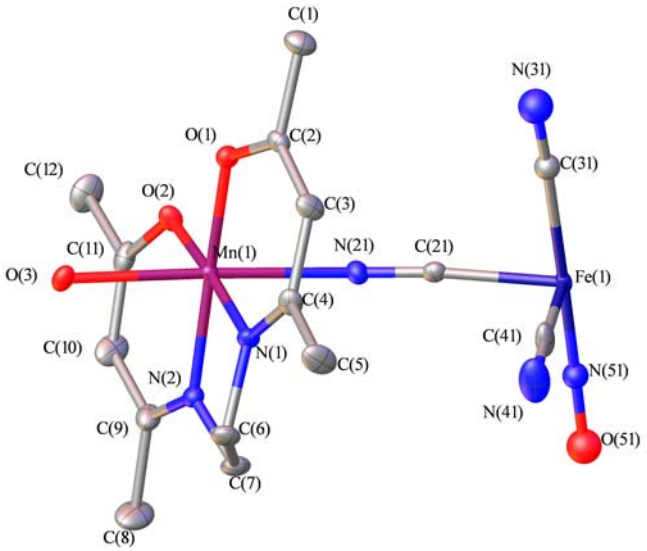

Fig. 2aS ORTEP plot (ellipsoids of 50% probability) with numerating scheme for $[Mn(acacen)H_2O]_2[Fe(CN)_5NO]$ in **2**.

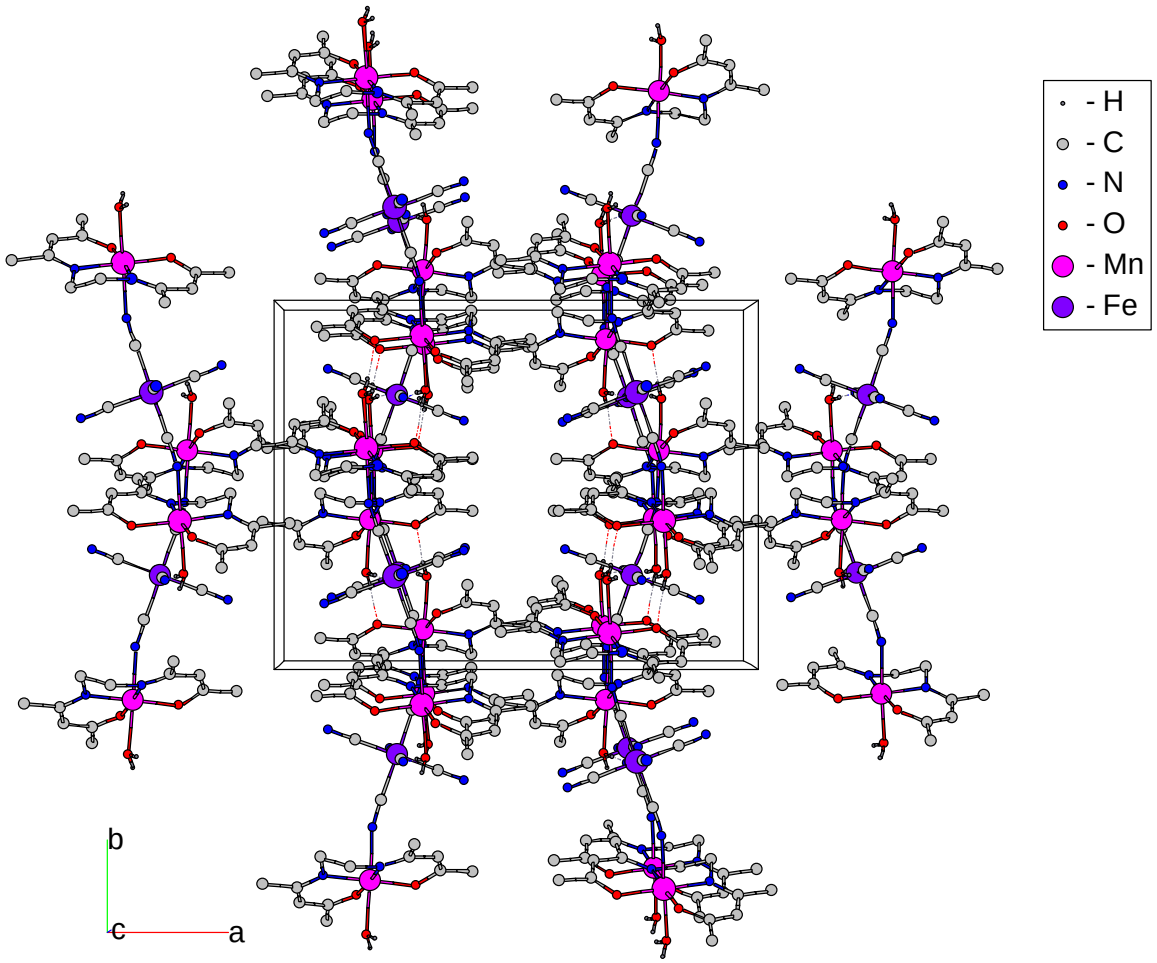

Fig. 2bS Molecular crystal packing (b) in [{Mn(acacen)H_2O}$_2$Fe(CN)$_5$NO] in **2**. Hydrogen atoms for *acacen* ligands and EtOH solvent molecules are omitted for clarity. Hydrogen bonds are shown by dashed lines.

Compound 3: [{Mn(acacen)H_2O}$_4$(Fe(CN)$_5$NO][Fe(CN)$_5$NO]·4CH_3CN

Table 3S. Selected geometric parameters (Å, º) in **3**.

Mn1—O1	1.8970 (10)	C2—C3	1.372 (2)
Mn1—O2	1.9082 (10)	C3—C4	1.423 (2)
Mn1—N2	1.9697 (12)	C4—C5	1.510 (2)
Mn1—N1	1.9710 (13)	C6—C7	1.512 (2)
Mn1—O3	2.2471 (11)	C8—C9	1.512 (2)
Mn1—N13	2.3325 (13)	C9—C10	1.431 (2)
Fe1—N4	1.658 (3)	C10—C11	1.371 (2)
Fe1—C13^{i}	1.9337 (14)	C11—C12	1.502 (2)
Fe1—C13^{ii}	1.9337 (14)	Fe2—Fe2^{iv}	0.5418 (12)
Fe1—C13	1.9337 (14)	Fe2—C21	1.532 (3)
Fe1—C13^{iii}	1.9337 (14)	Fe2—C22	1.9438 (16)
Fe1—C15	1.945 (3)	Fe2—C22^{v}	1.9438 (16)
N13—C13	1.1467 (19)	Fe2—C22^{iv}	1.9640 (16)
O4—N4	1.146 (4)	Fe2—C22^{vi}	1.9640 (16)
N15—C15	1.147 (4)	Fe2—C21^{iv}	2.073 (3)
O1—C2	1.2982 (19)	Fe2—N21N^{iv}	2.073 (3)
O2—C11	1.3036 (18)	C21—N21	1.154 (4)
N1—C4	1.308 (2)	C21—Fe2^{iv}	2.073 (3)
N1—C6	1.4774 (19)	N22—C22	1.147 (2)
N2—C9	1.300 (2)	C22—Fe2^{iv}	1.9640 (16)
N2—C7	1.4732 (19)	N1S—C1S	1.142 (3)
C1—C2	1.504 (2)	C1S—C2S	1.454 (4)
O1—Mn1—O2	90.58 (4)	O1—C2—C3	124.68 (14)
O1—Mn1—N2	176.26 (5)	O1—C2—C1	114.46 (14)
O2—Mn1—N2	92.63 (5)	N1—C4—C5	120.17 (14)
O1—Mn1—N1	92.60 (5)	C3—C4—C5	117.13 (15)

O2—Mn1—N1	175.13 (5)	N1—C6—C7	108.94 (12)
N2—Mn1—N1	84.33 (5)	N2—C7—C6	108.58 (12)
O1—Mn1—O3	90.39 (4)	C3—C2—C1	120.86 (15)
O2—Mn1—O3	91.31 (4)	C2—C3—C4	126.03 (15)
N2—Mn1—O3	87.62 (5)	N1—C4—C3	122.69 (14)
N1—Mn1—O3	92.36 (5)	N2—C9—C10	122.23 (13)
O1—Mn1—N13	93.49 (4)	N2—C9—C8	121.14 (14)
O2—Mn1—N13	87.44 (4)	C10—C9—C8	116.62 (14)
N2—Mn1—N13	88.57 (5)	C11—C10—C9	125.74 (15)
N1—Mn1—N13	88.68 (5)	O2—C11—C10	125.25 (14)
O3—Mn1—N13	175.93 (5)	O2—C11—C12	114.16 (13)
N4—Fe1—C13^{i}	96.11 (5)	C10—C11—C12	120.56 (14)
N4—Fe1—C13^{ii}	96.11 (5)	C21—Fe2—C22	95.84 (6)
C13^{i}—Fe1—C13^{ii}	89.352 (10)	C21—Fe2—C22^{v}	95.84 (6)
N4—Fe1—C13	96.11 (5)	C22—Fe2—C22^{v}	168.32 (12)
C13^{i}—Fe1—C13	89.352 (10)	C21—Fe2—C22^{iv}	100.09 (6)
C13^{ii}—Fe1—C13	167.79 (9)	C22—Fe2—C22^{iv}	88.979 (7)
N4—Fe1—C13^{iii}	96.11 (5)	C22^{v}—Fe2—C22^{iv}	88.979 (7)
C13^{i}—Fe1—C13^{iii}	167.79 (9)	C21—Fe2—C22^{vi}	100.09 (6)
C13^{ii}—Fe1—C13^{iii}	89.352 (10)	C22—Fe2—C22^{vi}	88.979 (7)
C13—Fe1—C13^{iii}	89.352 (11)	C22^{v}—Fe2—C22^{vi}	88.979 (7)
N4—Fe1—C15	180.000 (2)	C22^{iv}—Fe2—C22^{vi}	159.83 (12)
C13^{i}—Fe1—C15	83.89 (5)	C21—Fe2—C21^{iv}	180.000 (1)
C13^{ii}—Fe1—C15	83.89 (5)	C22—Fe2—C21^{iv}	84.16 (6)
C13—Fe1—C15	83.89 (5)	C22^{v}—Fe2—C21^{iv}	84.16 (6)
C13^{iii}—Fe1—C15	83.89 (5)	C22^{iv}—Fe2—C21^{iv}	79.91 (6)
C13—N13—Mn1	142.86 (11)	C22^{vi}—Fe2—C21^{iv}	79.91 (6)
N13—C13—Fe1	175.96 (14)	C21—Fe2—N21N^{iv}	180.000 (1)
O4—N4—Fe1	180.000 (2)	C22—Fe2—N21N^{iv}	84.16 (6)
N15—C15—Fe1	180.000 (1)	C22^{v}—Fe2—N21N^{iv}	84.16 (6)
C2—O1—Mn1	127.76 (10)	C22^{iv}—Fe2—N21N^{iv}	79.91 (6)
C11—O2—Mn1	125.95 (9)	C22^{vi}—Fe2—N21N^{iv}	79.91 (6)
C4—N1—C6	120.78 (13)	N21—C21—Fe2	180.000 (1)
C4—N1—Mn1	125.91 (10)	N21—C21—Fe2^{iv}	180.000 (1)
C6—N1—Mn1	112.57 (10)	N22—C22—Fe2	167.85 (18)
C9—N2—C7	122.08 (12)	N22—C22—Fe2^{iv}	176.18 (18)
C9—N2—Mn1	126.38 (10)	Fe2—C22—Fe2^{iv}	15.93 (4)
C7—N2—Mn1	111.25 (10)	N1S—C1S—C2S	178.6 (3)

Symmetry code(s): (i) *y*, -*x*+3/2, *z*; (ii) -*x*+3/2, -*y*+3/2, *z*; (iii) -*y*+3/2, *x*, *z*; (iv) *y*+1/2, -*x*+1, -*z*+2; (v) -*x*+3/2, -*y*+1/2, *z*; (vi) -*y*+1, *x*-1/2, -*z*+2.

Hydrogen bonds (Å, º) **in 3.**

Hydrogen bond	D-H	H...A	D...A	<(DHA)	Symmetry operations
O(3)-H(32)...O(2)	0.79(2)	2.01(2)	2.7894(14)	171(2)	-x+2, -y+1, -z+2
O(3)-H(31)...N(22)	0.84(3)	2.04(2)	2.8510(19)	162(2)	x, y, z

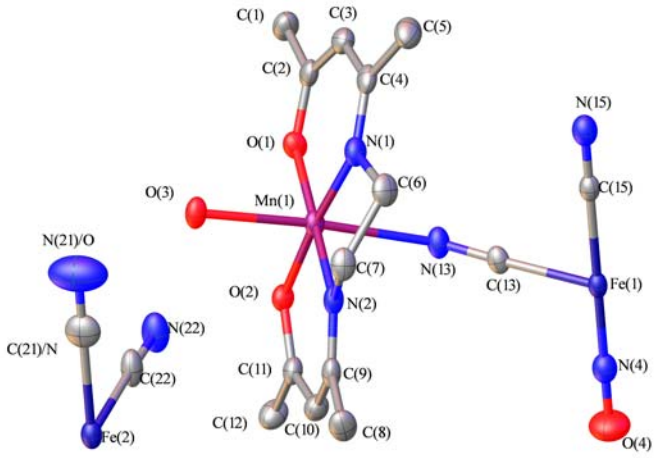

Fig. 3aS ORTEP plot (ellipsoids of 50% probability) with numerating scheme in **3**.

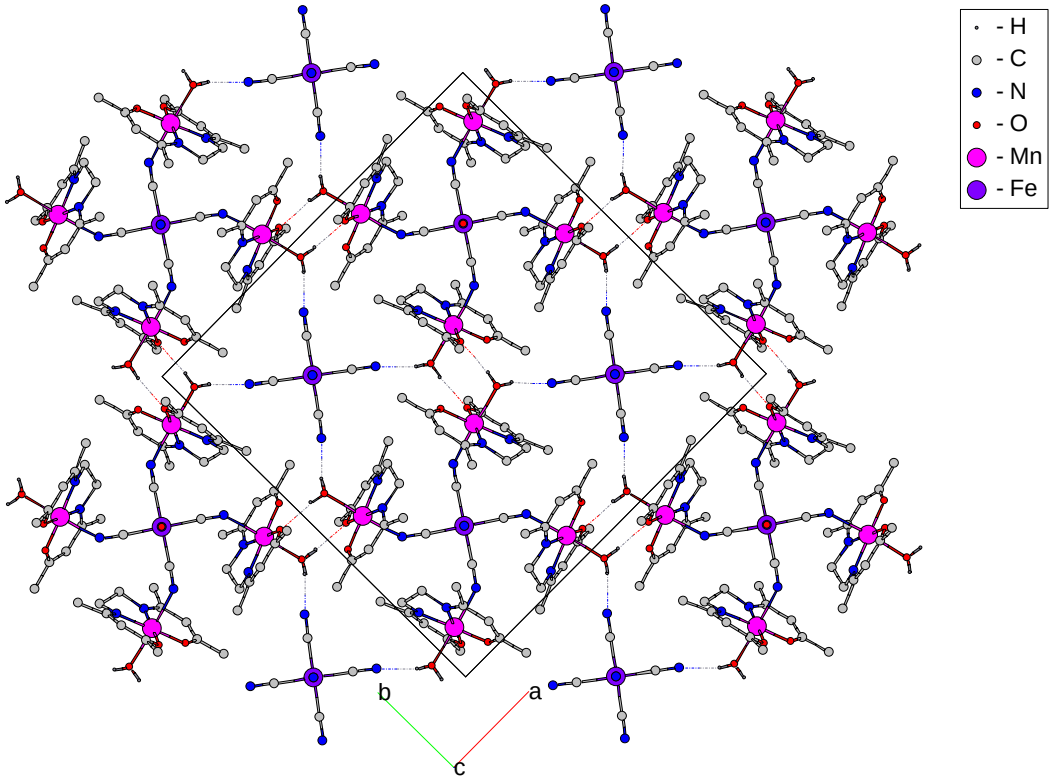

Fig. 3bS The layer based on hydrogen bonding between cations and anions in **3**

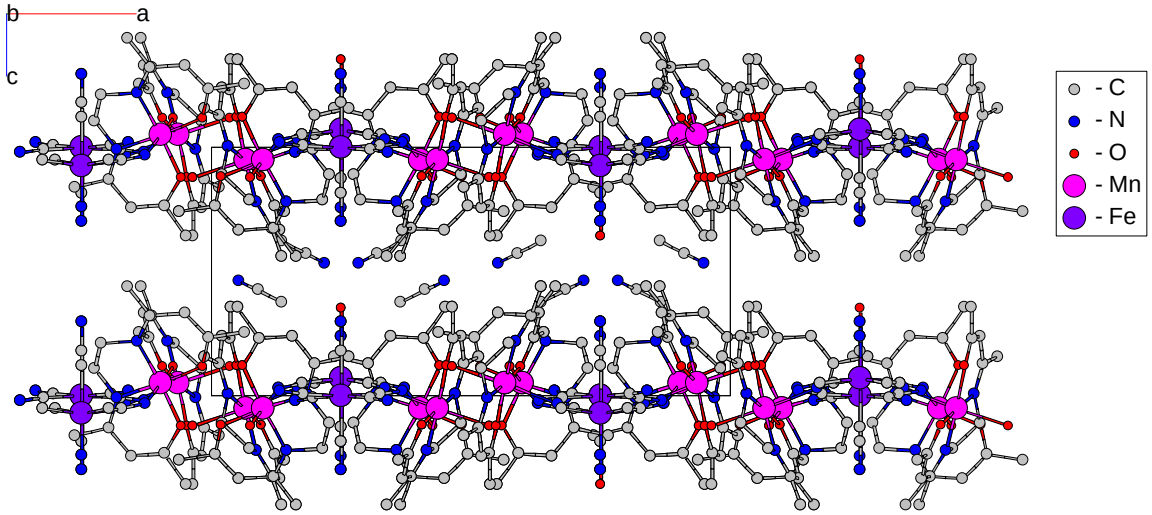

Fig. 3cS Superposition of the layers in **3**. Hydrogen atoms for acacen ligands are omitted for clarity.

Compound 4: $[\{Mn(acacen)\}_2(C_3H_7OH)\{Fe(CN)_5NO\}]_n$

Table 4S. Selected geometric parameters (Å, º) in **4**.

Mn1—O3	2.263 (2)	Fe1—C21	1.947 (4)
Mn1—N1	1.979 (2)	Fe1—C21^{i}	1.917 (4)
Mn1—N2	1.972 (2)	Fe1—C31	1.971 (10)
Mn1—O1	1.915 (2)	Fe1—C31^{i}	1.534 (9)
Mn1—O2	1.9004 (19)	Fe1—N51	1.632 (8)
Mn1—N21	2.267 (2)	Fe1—N51^{i}	2.078 (8)
N1—C4	1.305 (4)	Fe1—C41	1.914 (4)
N1—C6	1.475 (3)	Fe1—C41^{i}	1.969 (4)
N2—C7	1.471 (4)	N21—C21	1.147 (4)
N2—C9	1.311 (4)	C21—Fe1^{i}	1.917 (4)
C1—C2	1.504 (4)	C31—Fe1^{i}	1.534 (9)
C2—C3	1.366 (4)	C31—N31	1.176 (12)
C2—O1	1.313 (3)	C31—O51^{i}	1.271 (11)
C3—C4	1.429 (4)	N31—N51^{i}	1.122 (11)
C4—C5	1.505 (4)	N51—Fe1^{i}	2.078 (8)
C6—C7	1.518 (4)	N51—N31^{i}	1.122 (11)
C8—C9	1.510 (4)	N51—O51	1.129 (9)

C9—C10	1.421 (4)	O51—C31^{i}	1.271 (11)
C10—C11	1.376 (4)	C41—Fe1^{i}	1.969 (4)
C11—C12	1.501 (4)	C41—N41	1.146 (4)
C11—O2	1.301 (4)	O1S—C1S	1.318 (7)
Fe1—Fe1^{i}	0.448 (2)	C1S—C1S^{ii}	1.489 (10)
O3—Mn1—N21	178.19 (8)	Fe1^{i}—Fe1—N51	172.5 (10)
N1—Mn1—O3	91.06 (9)	Fe1^{i}—Fe1—C41^{i}	76.4 (8)
N1—Mn1—N21	87.85 (9)	Fe1^{i}—Fe1—C41	90.5 (8)
N2—Mn1—O3	87.35 (9)	C21^{i}—Fe1—C21	166.70 (7)
N2—Mn1—N1	83.75 (10)	C21^{i}—Fe1—C31	82.8 (3)
N2—Mn1—N21	91.10 (9)	C21—Fe1—C31	84.1 (3)
O1—Mn1—O3	92.03 (8)	C21—Fe1—N51^{i}	84.0 (2)
O1—Mn1—N1	92.19 (9)	C21^{i}—Fe1—N51^{i}	82.7 (3)
O1—Mn1—N2	175.88 (9)	C21^{i}—Fe1—C41^{i}	88.38 (17)
O1—Mn1—N21	89.46 (8)	C21—Fe1—C41^{i}	88.49 (17)
O2—Mn1—O3	88.21 (8)	C31^{i}—Fe1—C21^{i}	98.4 (4)
O2—Mn1—N1	176.05 (9)	C31^{i}—Fe1—C21	94.6 (4)
O2—Mn1—N2	92.33 (9)	C31^{i}—Fe1—C31	176.7 (2)
O2—Mn1—O1	91.72 (8)	C31^{i}—Fe1—N51^{i}	170.4 (5)
O2—Mn1—N21	92.77 (9)	C31^{i}—Fe1—C41^{i}	90.3 (4)
C4—N1—Mn1	125.77 (19)	C31^{i}—Fe1—C41	102.8 (4)
C4—N1—C6	122.2 (2)	N51—Fe1—C21	94.8 (3)
C6—N1—Mn1	112.05 (18)	N51—Fe1—C21^{i}	98.5 (3)
C7—N2—Mn1	111.93 (18)	N51—Fe1—C31	174.4 (5)
C9—N2—Mn1	125.5 (2)	N51—Fe1—N51^{i}	178.4 (2)
C9—N2—C7	122.5 (2)	N51—Fe1—C41	94.3 (3)
C3—C2—C1	121.0 (3)	N51—Fe1—C41^{i}	98.8 (3)
O1—C2—C1	114.4 (2)	C41—Fe1—C21^{i}	91.01 (18)
O1—C2—C3	124.6 (3)	C41—Fe1—C21	89.11 (17)
C2—C3—C4	126.6 (3)	C41—Fe1—C31	80.2 (3)
N1—C4—C3	121.9 (3)	C41^{i}—Fe1—C31	86.7 (3)
N1—C4—C5	121.1 (3)	C41^{i}—Fe1—N51^{i}	80.1 (2)
C3—C4—C5	117.0 (3)	C41—Fe1—N51^{i}	86.7 (2)
N1—C6—C7	107.4 (2)	C41—Fe1—C41^{i}	166.84 (7)
N2—C7—C6	108.1 (2)	C21—N21—Mn1	155.5 (2)
N2—C9—C8	120.7 (3)	Fe1^{i}—C21—Fe1	13.30 (7)
N2—C9—C10	122.5 (3)	N21—C21—Fe1	172.3 (3)
C10—C9—C8	116.8 (3)	N21—C21—Fe1^{i}	174.4 (3)
C11—C10—C9	125.8 (3)	Fe1^{i}—C31—Fe1	3.3 (2)
C10—C11—C12	121.2 (3)	N31—C31—Fe1^{i}	179.2 (9)
O2—C11—C10	124.9 (3)	N31—C31—Fe1	177.0 (7)
O2—C11—C12	113.9 (3)	N31^{i}—N51—Fe1	159.1 (7)
C2—O1—Mn1	125.10 (17)	N31^{i}—N51—Fe1^{i}	158.1 (7)
C11—O2—Mn1	126.10 (19)	O51—N51—Fe1^{i}	178.0 (7)
Fe1^{i}—Fe1—C21	79.5 (8)	O51—N51—Fe1	178.0 (7)
Fe1^{i}—Fe1—C21^{i}	87.2 (8)	N41—C41—Fe1^{i}	173.3 (3)
Fe1^{i}—Fe1—C31	11.2 (8)	N41—C41—Fe1	173.5 (3)
Fe1^{i}—Fe1—C31^{i}	165.5 (10)	O1S—C1S—C1S^{ii}	110.8 (4)

Symmetry code(s): (i) -*x*+3/2, -*y*-1/2, -*z*; (ii) -*x*+1, *y*, -*z*+1/2.

Hydrogen bonds (Å, º) **in 4**

Hydrogen bond	D-H	H...A	D...A	<(DHA)	Symmetry operations
O(1s)-H(1)...N(81)	0.84(4)	2.10(4)	2.936(4)	175(4)	-x+2, y+1/2, -z+1

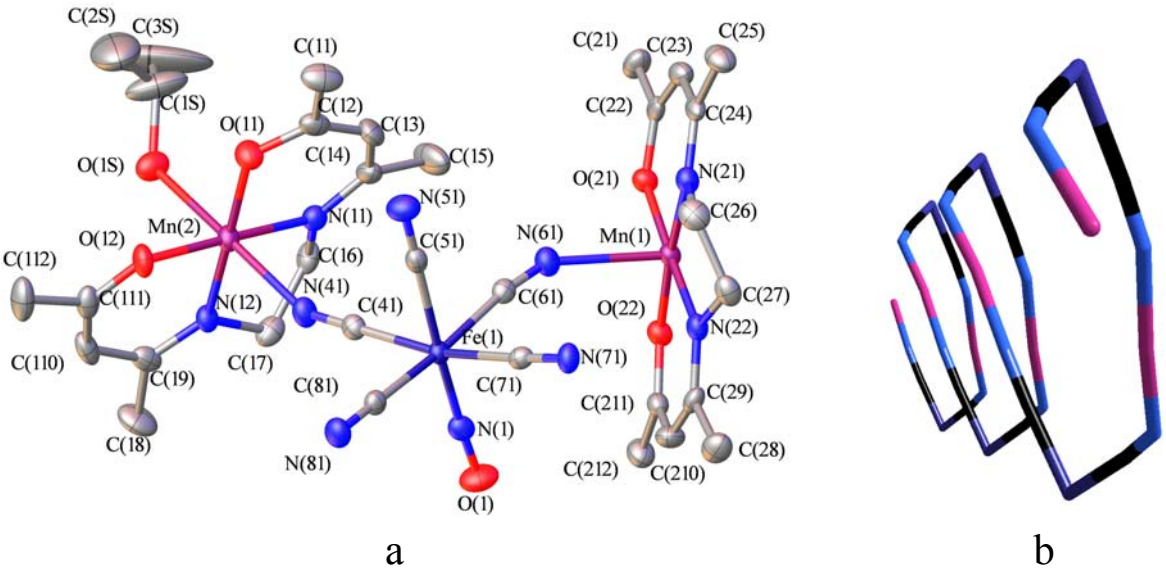

Fig. 4S. ORTEP plot (ellipsoids of 50% probability) with numerating scheme (a), simplified backbone of the right-handed helical chain (b, view along 2_1 axis).

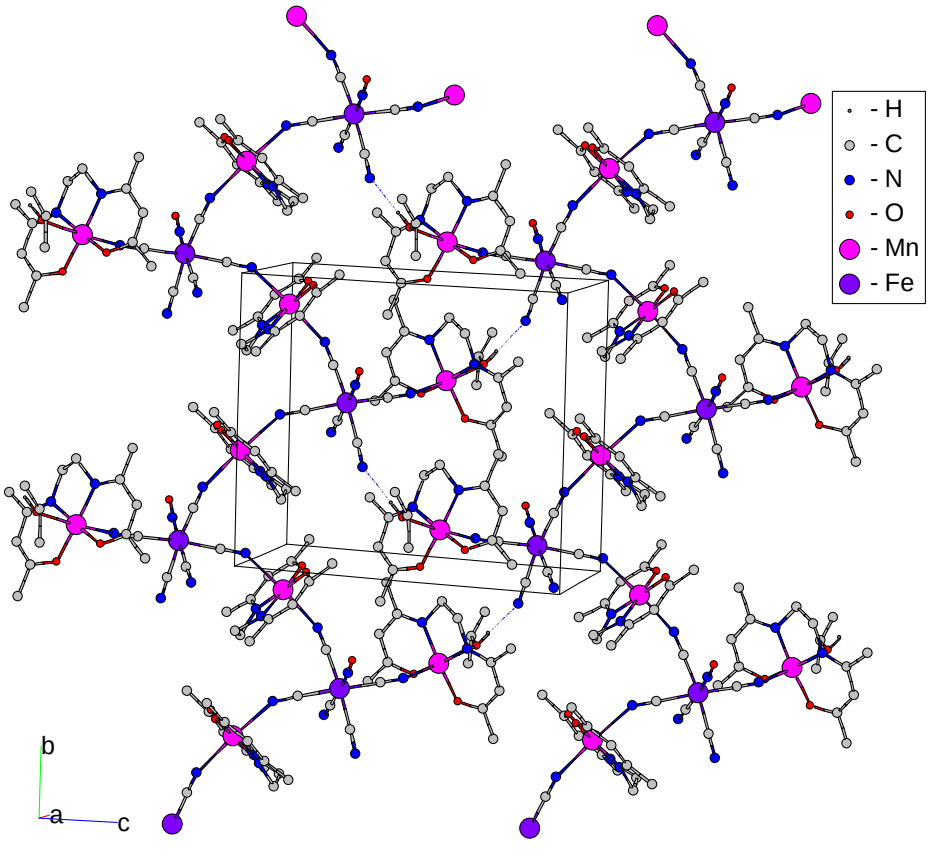

Fig. 4bS Packing of the chains (c) in $[\{Mn(acacen)\}_2(i\text{-}PrOH)\{Fe(CN)_5NO\}]_n$ (**4**). Hydrogen atoms of SB ligands are omitted for clarity. Hydrogen bonds are shown by dashed lines.

Compound 5: $[\{Mn(acacen)\}_2Fe(CN)_5NO]_n$

Table 5S. Selected geometric parameters (Å, º) in **5**.

Fe1—N16	1.644 (3)	C106—C107	1.497 (5)
Fe1—C15	1.923 (4)	C107—N102	1.472 (4)
Fe1—C11	1.942 (3)	N102—C109	1.313 (4)
Fe1—C12	1.953 (3)	C108—C109	1.503 (5)
Fe1—C14	1.966 (3)	C109—C110	1.402 (5)
Fe1—C13	1.966 (3)	C110—C111	1.362 (5)
C11—N11	1.150 (4)	C111—O102	1.297 (4)
N11—Mn1	2.375 (3)	C111—C112	1.495 (5)
C12—N12	1.143 (4)	Mn2—O202	1.896 (2)
N12—Mn2	2.441 (3)	Mn2—O201	1.892 (2)
C13—N13	1.132 (4)	Mn2—N202	1.959 (3)

N13—Mn2^{i}	2.437 (3)	Mn2—N201	1.978 (3)
C14—N14	1.145 (4)	Mn2—N13^{iv}	2.437 (3)
N14—Mn1^{ii}	2.450 (3)	O201—C202	1.301 (4)
C15—N15	1.150 (5)	C201—C202	1.510 (6)
N16—O16	1.132 (4)	C202—C203	1.352 (6)
Mn1—O102	1.895 (2)	C203—C204	1.398 (6)
Mn1—O101	1.901 (2)	C204—N201	1.297 (4)
Mn1—N102	1.969 (3)	C204—C205	1.531 (5)
Mn1—N101	1.972 (3)	N201—C206	1.462 (5)
Mn1—N14^{iii}	2.450 (3)	C206—C207	1.449 (6)
O101—C102	1.301 (4)	C207—N202	1.454 (5)
C101—C102	1.499 (5)	N202—C209	1.318 (4)
C102—C103	1.363 (5)	C208—C209	1.509 (5)
C103—C104	1.408 (5)	C209—C210	1.401 (5)
C104—N101	1.310 (4)	C210—C211	1.350 (5)
C104—C105	1.517 (5)	C211—O202	1.300 (4)
N101—C106	1.464 (4)	C211—C212	1.502 (5)
N16—Fe1—C15	175.29 (15)	N102—C107—C106	107.2 (3)
N16—Fe1—C11	92.93 (14)	C109—N102—C107	122.7 (3)
C15—Fe1—C11	82.49 (14)	C109—N102—Mn1	125.4 (2)
N16—Fe1—C12	93.19 (15)	C107—N102—Mn1	111.9 (2)
C15—Fe1—C12	85.73 (15)	N102—C109—C110	121.8 (3)
C11—Fe1—C12	90.15 (12)	N102—C109—C108	120.3 (3)
N16—Fe1—C14	97.07 (14)	C110—C109—C108	117.9 (3)
C15—Fe1—C14	87.52 (14)	C111—C110—C109	126.6 (3)
C11—Fe1—C14	169.95 (15)	O102—C111—C110	124.3 (3)
C12—Fe1—C14	90.20 (12)	O102—C111—C112	114.0 (3)
N16—Fe1—C13	92.45 (15)	C110—C111—C112	121.7 (3)
C15—Fe1—C13	88.56 (15)	C111—O102—Mn1	125.4 (2)
C11—Fe1—C13	88.57 (13)	O202—Mn2—O201	93.27 (10)
C12—Fe1—C13	174.27 (15)	O202—Mn2—N202	91.58 (11)
C14—Fe1—C13	90.09 (12)	O201—Mn2—N202	174.86 (12)
N11—C11—Fe1	178.0 (3)	O202—Mn2—N201	174.55 (11)
C11—N11—Mn1	161.3 (3)	O201—Mn2—N201	92.15 (11)
N12—C12—Fe1	177.5 (3)	N202—Mn2—N201	83.01 (12)
C12—N12—Mn2	158.9 (3)	O202—Mn2—N13^{iv}	92.30 (10)
N13—C13—Fe1	173.9 (3)	O201—Mn2—N13^{iv}	84.37 (10)
C13—N13—Mn2^{i}	156.2 (3)	N202—Mn2—N13^{iv}	97.11 (11)
N14—C14—Fe1	177.9 (3)	N201—Mn2—N13^{iv}	87.75 (11)
C14—N14—Mn1^{ii}	160.6 (3)	O202—Mn2—N12	84.40 (9)
N15—C15—Fe1	175.8 (3)	O201—Mn2—N12	92.23 (10)
O16—N16—Fe1	176.0 (3)	N202—Mn2—N12	86.58 (11)
O102—Mn1—O101	93.27 (10)	N201—Mn2—N12	95.88 (11)
O102—Mn1—N102	91.56 (10)	N13^{iv}—Mn2—N12	175.13 (11)
O101—Mn1—N102	175.17 (10)	C202—O201—Mn2	123.6 (2)
O102—Mn1—N101	174.44 (11)	O201—C202—C203	126.0 (3)
O101—Mn1—N101	91.77 (11)	O201—C202—C201	112.5 (4)
N102—Mn1—N101	83.41 (11)	C203—C202—C201	121.5 (4)
O102—Mn1—N11	91.76 (9)	C202—C203—C204	125.9 (3)
O101—Mn1—N11	86.46 (10)	N201—C204—C203	122.5 (3)
N102—Mn1—N11	93.48 (11)	N201—C204—C205	120.3 (4)
N101—Mn1—N11	86.20 (10)	C203—C204—C205	117.1 (3)
O102—Mn1—N14^{iii}	83.49 (9)	C204—N201—C206	123.8 (3)
O101—Mn1—N14^{iii}	90.25 (10)	C204—N201—Mn2	125.0 (3)
N102—Mn1—N14^{iii}	90.22 (11)	C206—N201—Mn2	111.1 (2)
N101—Mn1—N14^{iii}	98.85 (10)	C207—C206—N201	108.9 (3)
N11—Mn1—N14^{iii}	174.06 (10)	N202—C207—C206	108.7 (3)
C102—O101—Mn1	125.7 (2)	C209—N202—C207	123.6 (3)
O101—C102—C103	124.4 (3)	C209—N202—Mn2	124.2 (2)
O101—C102—C101	114.3 (3)	C207—N202—Mn2	111.6 (2)
C103—C102—C101	121.3 (3)	N202—C209—C210	122.1 (3)
C102—C103—C104	126.6 (3)	N202—C209—C208	121.0 (4)
N101—C104—C103	122.3 (3)	C210—C209—C208	116.9 (3)
N101—C104—C105	121.4 (4)	C211—C210—C209	126.3 (3)

C103—C104—C105	116.3 (3)	O202—C211—C210	125.1 (3)
C104—N101—C106	122.8 (3)	O202—C211—C212	114.1 (3)
C104—N101—Mn1	125.2 (3)	C210—C211—C212	120.8 (3)
C106—N101—Mn1	111.8 (2)	C211—O202—Mn2	124.5 (2)
N101—C106—C107	108.4 (3)		

Symmetry code(s): (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*-1, *y*, *z*; (iv) *x*, *y*-1, *z*.

No hydrogen bonds found in 5.

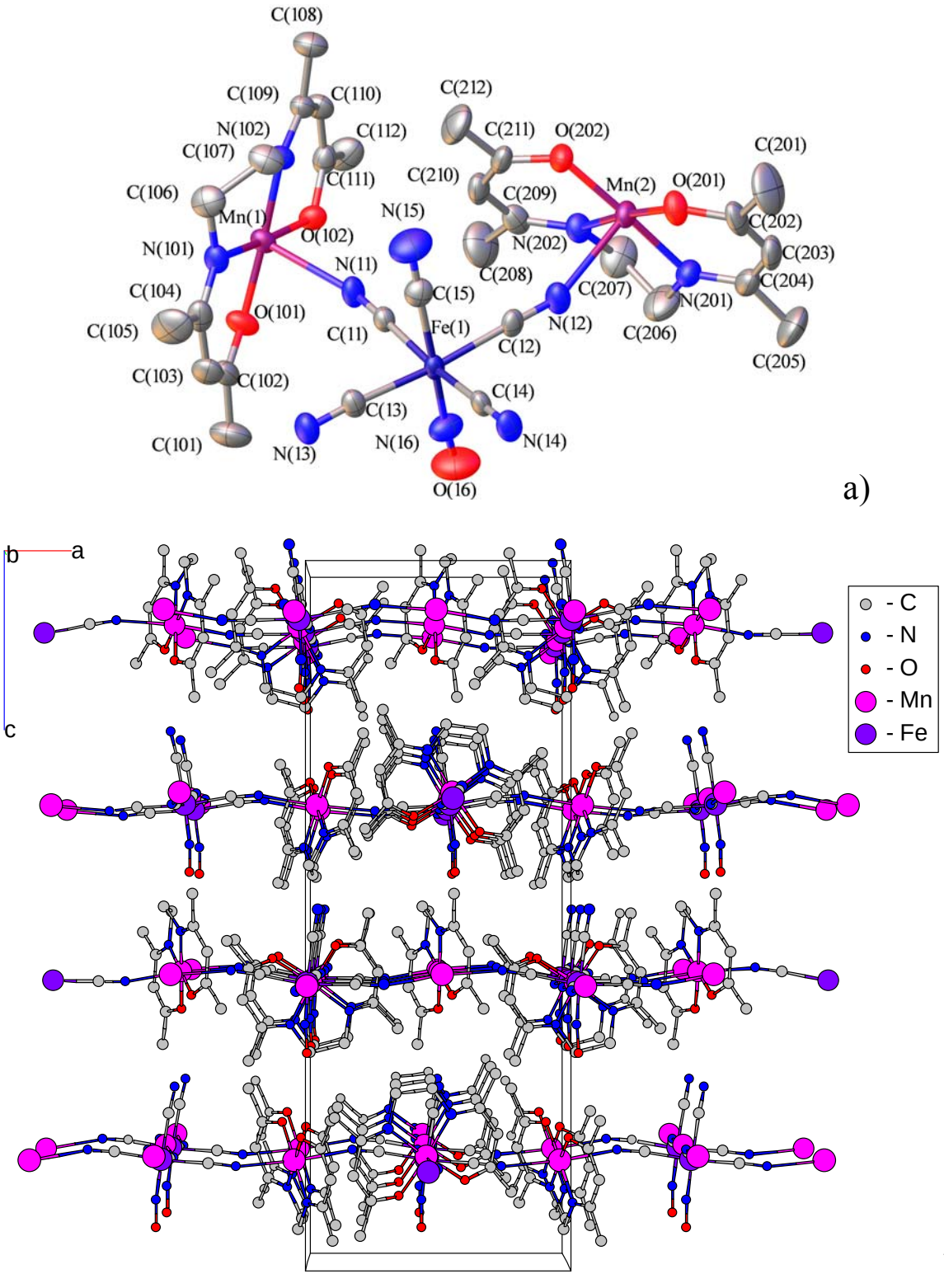

Fig. 5S ORTEP plot (ellipsoids of 50% probability) with numerating scheme (a) and four layered packing as a result of 4_3 screw axis (b) in crystal structure of $[\{Mn(acacen)\}_2Fe(CN)_5NO]_n$ (**5**).

IR spectra, DSC and magnetic measurements

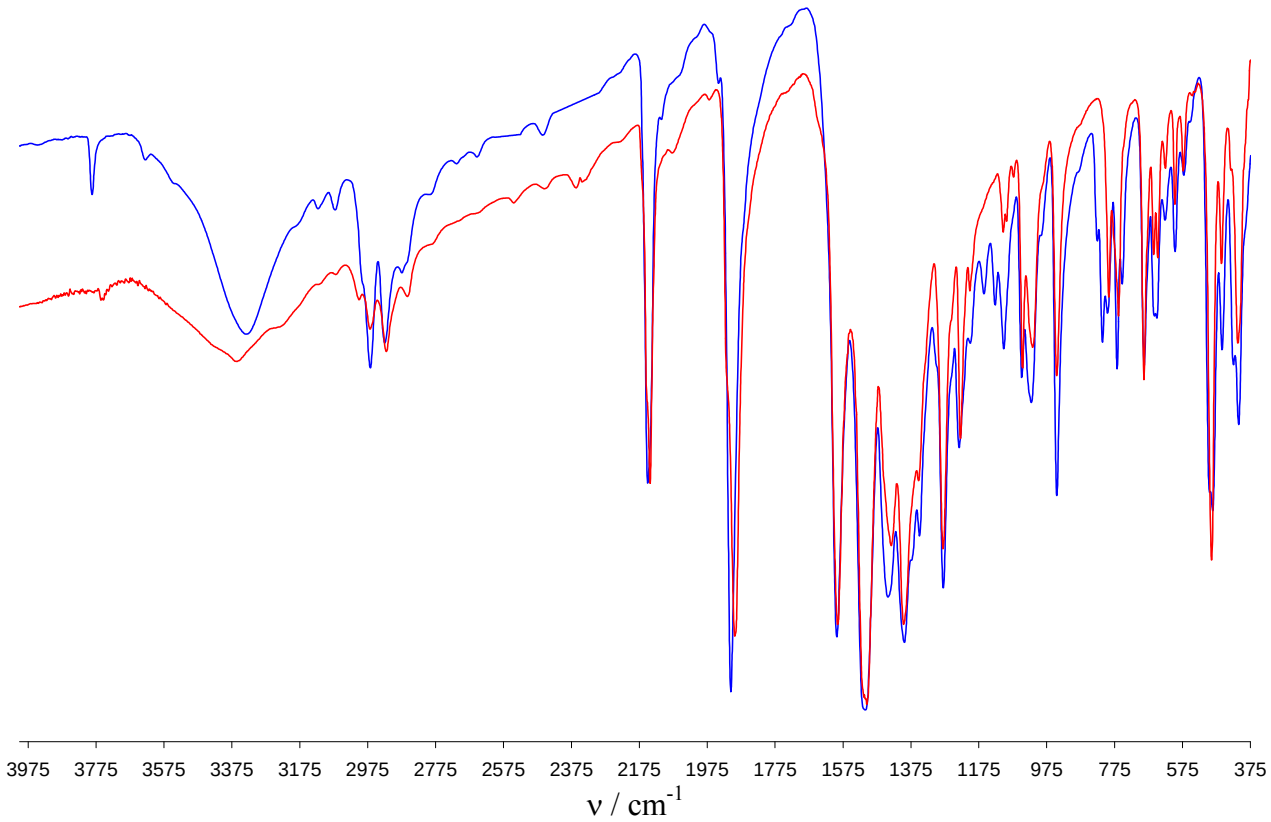

Fig. 6S IR (KBr): bleu - $[\{Mn(acacen)\}_2(i\text{-}PrOH)\{Fe(CN)_5NO\}]_n$,**4**; red - $[Mn(acacen)(MeOH)]_2[Fe(CN)_5NO]\cdot 1.5MeOH$, **5**

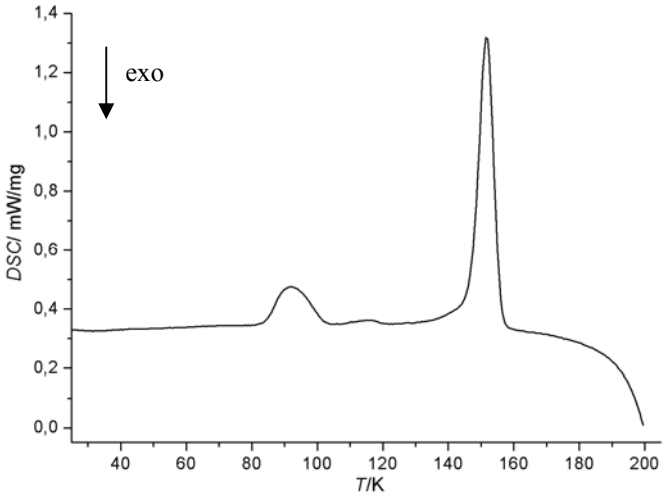

Fig. 7S DSC for $[\{Mn(acacen)\}_2(i\text{-}PrOH)\{Fe(CN)_5NO\}]_n$ (**4**).

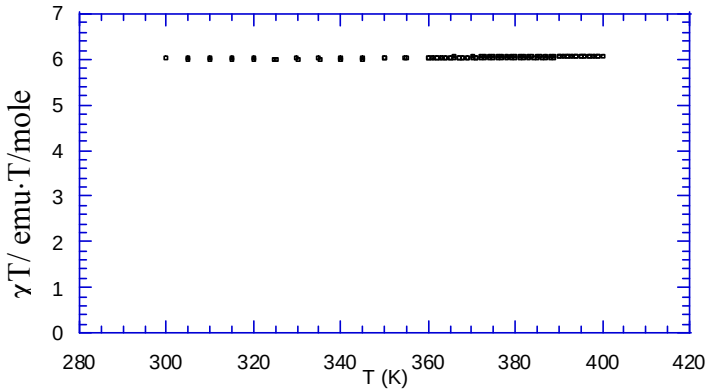

Fig. 8S Magnetic measurements at high temperature for $[\{Mn(acacen)\}_2(i\text{-}PrOH)\{Fe(CN)_5NO\}]_n$ (**4**).
Magnetic susceptibility data were collected on going up 305 K up to 400 and than on going down 400 up to 300 K.