

Supplementary Material Ghazzali et al.

Experimental details

Preparations Caution: Perchlorate salts of metal complexes are potentially explosive. Only small quantities of the compound should be prepared and handled with care. At least two preparations and two independent crystal structure determinations were made for each compound. As a number of components have been used in these preparations, concomitant precipitation of other solids is a problem, for example salts of the ligand,^[20] or other combinations of the molecular entities present.^[21]

Tris(1,10-phenanthroline)iron(II)chloride,^[22] tris(1,10-phenanthroline) iron(II)perchlorate hydrate,^[22] tris(1,10-phenanthroline)ruthenium(II) chloride^[23] and 1,2-bis(4-pyridylmethylene)hydrazine^[24] were prepared, with minor modifications, according to the literature.

1 A solution of tris(1,10-phenanthroline) iron(II)chloride (0.2 mmol, 0.13 g) in 10 ml MeOH/MeCN (1:1) was added dropwise to a stirred methanolic solution of 1,2-bis(4-pyridylmethylene)hydrazine (0.4 mmol, 0.08 g), iron(II) perchlorate hexahydrate [0.2 mmol, 0.05 g] and potassium thiocyanate [0.4 mmol, 0.04 g]. The solution was allowed to stir under N₂ for 2 hours at room temperature then filtered off and allowed to stand for 1 week. Uniform bluish dark prismatic crystals of **1** were collected and dried in air. A small amount (4-5%) of co-precipitated KClO₄ could not be avoided IR: (γ , cm⁻¹, KBr): 501(m) [ν_{M-N}], 624(m) [SCN⁻], 730(m)[SCN⁻], 849(m)[SCN⁻], 1090(s)[ClO₄⁻], 1427(s)[$\delta_{C=N}$], 3524(s) [H₂O_{stretching}]. Analytical data for C₁₁₀H₉₀Cl_{4.85}Fe₃K_{0.85}N₂₆O_{25.4}S₂: Calc.: C, 50.44; H, 3.46; N, 13.91. Found: C, 50.80; H, 2.90; N, 13.90.

2 A solution of tris (1,10-phenanthroline) iron(II)perchlorate hydrate (0.2 mmol, 0.14 g) in 15 ml MeOH/EtOH/MeCN (1:1:1) is added dropwise to a stirred methanolic solution of 1,2-bis(4-pyridylmethylene)hydrazine (0.1 mmol, 0.02 g). The solution was allowed to stir for 2 hours at room temperature then filtered off and allowed to stand for 1 week. Red prisms of ([Fe(phen)₃]₂bphz(ClO₄)₄·nMeOH) **2** were collected and dried in air. IR: (γ , cm⁻¹, KBr): 509(m)[ν_{M-N}], 624(m)[C=C], 1085(s)[ClO₄⁻], 1425(s) [$\delta_{C=N}$].

3 A solution of tris(1,10-phenanthroline) ruthenium(II)chloride hydrate (0.2 mmol, 0.14 g) in 15 ml MeOH/EtOH/MeCN (1:1:1) is added dropwise to a stirred methanolic solution of 1,2-bis(4-pyridylmethylene)hydrazine (0.4 mmol, 0.08 g), iron(II) perchlorate hexahydrate [0.2 mmol, 0.05 g] and potassium thiocyanate [0.4 mmol, 0.04 g]. The solution was allowed to stir under N₂ for 2 hours at room temperature then filtered off and allowed to stand for 1 week. Reddish orange blocks of **3** were collected after 1 week and dried in air. IR: (γ , cm⁻¹, KBr): 512 (m) [ν_{M-N}], 742(m)[SCN⁻], 1150(s)[ClO₄⁻], 1405(s)[$\delta_{C=N}$].

X-ray diffraction Diffraction data for **1-3** were collected using a Siemens SMART CCD diffractometer with Mo-K α radiation ($\lambda=0.71073$ Å, graphite monochromator). The crystals were cooled to 153 K (**1,3**) and 173 K (**2**) by a flow of nitrogen gas using the LT-2A device. Full spheres of reciprocal space were scanned by 0.3 steps in ω with a crystal-to-detector distance of 3.97 cm. Preliminary orientation matrices were obtained from the first frames using SMART.^[25] The collected frames were integrated using the preliminary orientation matrices which were updated every 100 frames. Final cell parameters were obtained by refinement of the positions of reflections with $I > 10\sigma(I)$ after integration of all the frames using SAINT^[26]. The data were empirically corrected for absorption and other effects using the SADABS^[27] program. The structure was solved by direct methods and refined by full-matrix least squares on all $|F^2|$ data using SHELXTL software.^[28] While hydrogen atoms were refined isotropically with use of geometrical constraints, two disordered ClO₄⁻ as well as one disordered H₂O molecules in **1** and two disordered ClO₄⁻ as well as one disordered MeOH molecule in **2** could not be modelled properly and were squeezed out with PLATON^[29].

1 Moiety Formula: $C_{100}H_{86}Fe_3N_{26}S_2O_{20}Cl_4$, Mr=2465.52, Z=4, Monoclinic, Space group $P2_1/n$, $a=13.2081(6)$, $b=22.073(1)$, $c=18.8381(9)$ Å, $\alpha=\gamma=90^\circ$, $\beta=93.242(1)^\circ$, $V=5483.3(4)$ Å³, θ range=2.05-25.26°, Completeness to $\theta_{max}=99.5\%$, Data/restraints/parameters: 9889/2/652, Measured refl., 60159, Unique refl., 9889, $R_{int}=0.0627$, $R(I>2\sigma)=0.0480$, $wR_2(all)=0.1472$, $S=1.004$, Largest peak/hole: 0.587 / -0.269 e.Å⁻³ CCDC: 758946.

2 Moiety Formula: $C_{42.5}H_{31}Cl_2FeN_8O_{8.5}$, Mr=923.52, Z=2, Triclinic, Space group P-1 (no.2), $a=12.2473(4)$, $b=12.6914(5)$, $c=13.7110(5)$ Å, $\alpha=79.294(1)$, $\beta=74.263(1)$, $\gamma=69.511(1)^\circ$, $V=1911.75(12)$ Å³, θ range=2.07-30.00°, Completeness to $\theta_{max}=99.7\%$, Data/restraints/parameters: 11108/0/460, Measured refl. 30745, Unique refl., 11108, $R_{int}=0.035$, $R(I>2\sigma)=0.0492$, $wR_2(all)=0.1351$, $S=1.012$, Largest peak/hole: 0.472 / -0.284 e.Å⁻³ CCDC: 758947.

3 Monoclinic, Space group $P2_1/n$, $a=13.257(4)$, $b=22.684(8)$, $c=18.352(6)$ Å, $\alpha=\gamma=90^\circ$, $\beta=94.393(9)^\circ$, $V=5502.734(4)$ Å³. Complete refinement not possible due to low crystal quality.

Table S.1 Short intermolecular C...C contact distances in **1**. A: bridging ligand B: free ligand C, D and E: the three phenanthroline ligands.

Atom1	Atom2	Symm. op.	Length
C12C	C1A	-1/2+x,1/2-y,-1/2+z	3.6
C13A	C3C	1+x,y,1+z	3.587
C15A	C5A	1/2+x,1/2-y,1/2+z	3.595
C15A	C6D	x,y,1+z	3.563
C16A	C5D	x,y,1+z	3.397
C16A	C6D	x,y,1+z	3.431
C1A	C12C	1/2+x,1/2-y,1/2+z	3.6
C1B	C7E	x,y,z	3.459
C2B	C7E	x,y,z	3.466
C3A	C3C	1/2+x,1/2-y,1/2+z	3.561
C3C	C13A	-1+x,y,-1+z	3.587
C3C	C3A	-1/2+x,1/2-y,-1/2+z	3.561
C4C	C5A	-1/2+x,1/2-y,-1/2+z	3.506
C4C	C6A	-1/2+x,1/2-y,-1/2+z	3.533
C5A	C15A	-1/2+x,1/2-y,-1/2+z	3.595
C5A	C4C	1/2+x,1/2-y,1/2+z	3.506
C5D	C16A	x,y,-1+z	3.397
C5E	C6A	x,y,-1+z	3.492
C6A	C4C	1/2+x,1/2-y,1/2+z	3.533
C6A	C5E	x,y,1+z	3.492
C6D	C15A	x,y,-1+z	3.563
C6D	C16A	x,y,-1+z	3.431
C6D	C6D	1-x,1-y,1-z	3.21
C7B	C13E	x,y,z	3.521
C12C	C1A	-1/2+x,1/2-y,-1/2+z	3.6
C13A	C3C	1+x,y,1+z	3.587
C15A	C5A	1/2+x,1/2-y,1/2+z	3.595
C15A	C6D	x,y,1+z	3.563
C16A	C5D	x,y,1+z	3.397
C16A	C6D	x,y,1+z	3.431

Table S2. Short intermolecular C...N contact distances in **1**, A: bridging ligand B: free ligand C, D and E: the three phenanthroline ligands.

Atom1	Atom2	Symm. op.	Length
C3D	N4B	-1/2+x,1/2-y,-1/2+z	3.499
C5C	N4B	-1+x,y,z	3.552
C6C	N4B	-1+x,y,z	3.476
N8B	C8C	x,y,z	3.524
N8B	C9C	x,y,z	3.329

Table S3. Short intermolecular C...H or N...H contact distances in **1**, A: bridging ligand B: free ligand C, D and E: the three phenanthroline ligands.

Atom1	Atom2	Symm. op.	Length
H7B	C8C	1-x,-y,1-z	2.706
H3C	C13A	-1+x,y,-1+z	2.716
H7B	C9C	1-x,-y,1-z	2.895

Table S4. Short intermolecular C...C contact distances in **2**, B: free ligand

Atom1	Atom2	Symm. op.	Length
C18	C18	1-x,-y,1-z	3.373
C26	C29	1-x,1-y,1-z	3.507
C26	C30	1-x,1-y,1-z	3.399
C27	C28	1-x,1-y,1-z	3.583
C28	C28	1-x,1-y,1-z	3.47
C29	C26	1-x,1-y,1-z	3.507
C30	C26	1-x,1-y,1-z	3.399
C5	C9	2-x,1-y,-z	3.521
C6	C9	2-x,1-y,-z	3.564
C26	C37B	x,y,z	3.517
C27	C37B	x,y,z	3.545
C1	C41B	1+x,-1+y,z	3.592
C1	C42B	1+x,-1+y,z	3.47
C2	C41B	1+x,-1+y,z	3.535
C2	C42B	1+x,-1+y,z	3.55
C5	C42B	1-x,1-y,-z	3.517
C32	C39B	1+x,y,z	3.499

Table S5. Short intermolecular C...N contact distances in **2**, B: free ligand

Atom1	Atom2	Symm. op.	Length
C27	N7B	x,y,z	3.578
C13	N8B	1-x,1-y,-z	3.508
C3	N8B	1+x,-1+y,z	3.495
C4	N8B	1-x,1-y,-z	3.553
C21	N7B	1-x,1-y,1-z	3.49
C22	N7B	1-x,1-y,1-z	3.465

Table S6. Short intermolecular C...H or N...H contact distances in **2**, B: free ligand

Atom1	Atom2	Symm. op.	Length
C18	H40B	1+x,-1+y,z	2.836
C34	H8	2-x,1-y,-z	2.842
C22	H27	1-x,1-y,1-z	2.886
C24	H42B	1+x,-1+y,z	2.892
C26	H37B	x,y,z	2.751
H42B	C24	-1+x,1+y,z	2.892
C39B	H32	-1+x,y,z	2.825
C19	H40B	1+x,-1+y,z	2.826

Table S7. Fe...Fe distances in **1** and **2**

Comp. 1				Comp. 2			
Atom1	Atom2	Symm. op. 2	Length	Atom1	Atom2	Symm. op. 2	Length
Fe1	Fe2	1/2-x,-1/2+y,3/2-z	8.065	Fe1	Fe1	2-x,1-y,-z	9.076
Fe2	Fe1	1/2-x,1/2+y,3/2-z	8.065	Fe1	Fe1	1-x,1-y,1-z	9.168
Fe1	Fe2	1/2+x,1/2-y,1/2+z	8.065	Fe1	Fe1	2-x,-y,1-z	10.171
Fe1	Fe2	-1/2+x,1/2-y,1/2+z	9.758	Fe1	Fe1	2-x,-y,-z	10.34
Fe2	Fe1	3/2-x,1/2+y,3/2-z	9.758	Fe1	Fe1	1-x,1-y,-z	10.675
Fe1	Fe2	3/2-x,-1/2+y,3/2-z	9.758				
Fe2	Fe1	x,y,-1+z	10.301				
Fe1	Fe2	x,y,1+z	10.301				
Fe1	Fe2	1-x,-y,1-z	10.301				
Fe2	Fe2	1-x,-y,1-z	10.599				
Fe2	Fe2	1/2+x,1/2-y,1/2+z	11.22				
Fe2	Fe2	-1/2+x,1/2-y,-1/2+z	11.22				
Fe1	Fe2	1-x,-y,2-z	11.291				
Fe1	Fe2	x,y,z	11.291				
Fe2	Fe2	1/2+x,1/2-y,-1/2+z	11.83				
Fe2	Fe2	-1/2+x,1/2-y,1/2+z	11.83				

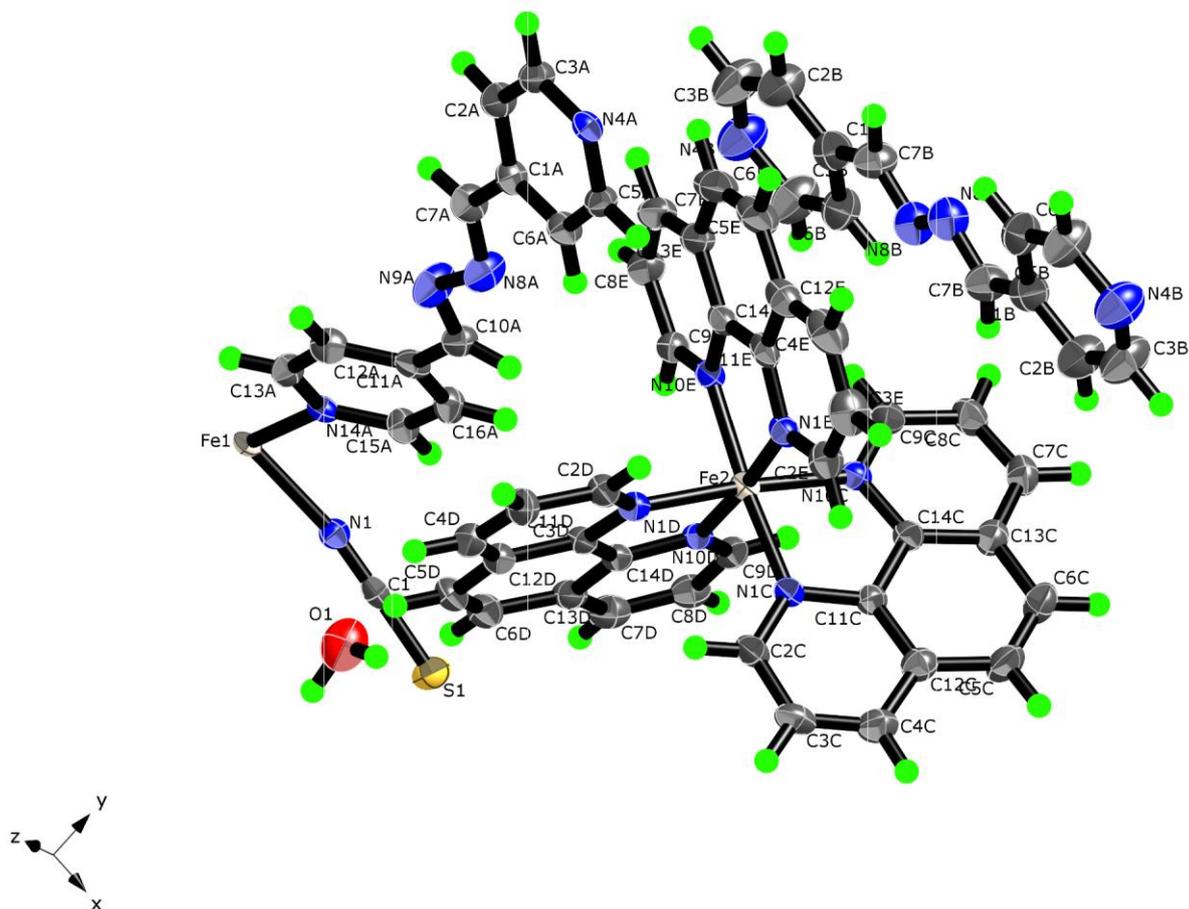


Figure S1. ORTEP type plot and atomic numbering for **1**

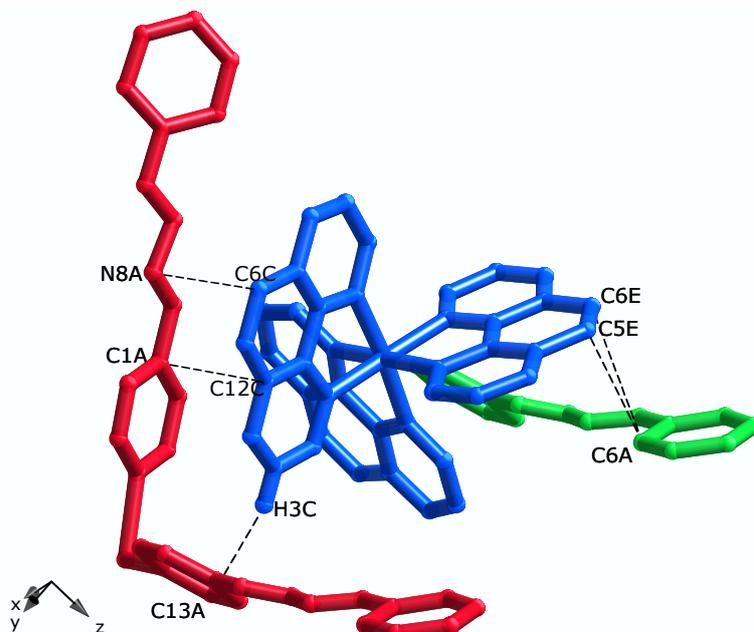


Figure S2. Some of the π - π and CH σ - π interactions defining the position of the $[\text{Fe}(\text{phen})_3]^{2+}$ vis-a-vis the grid in **1**.

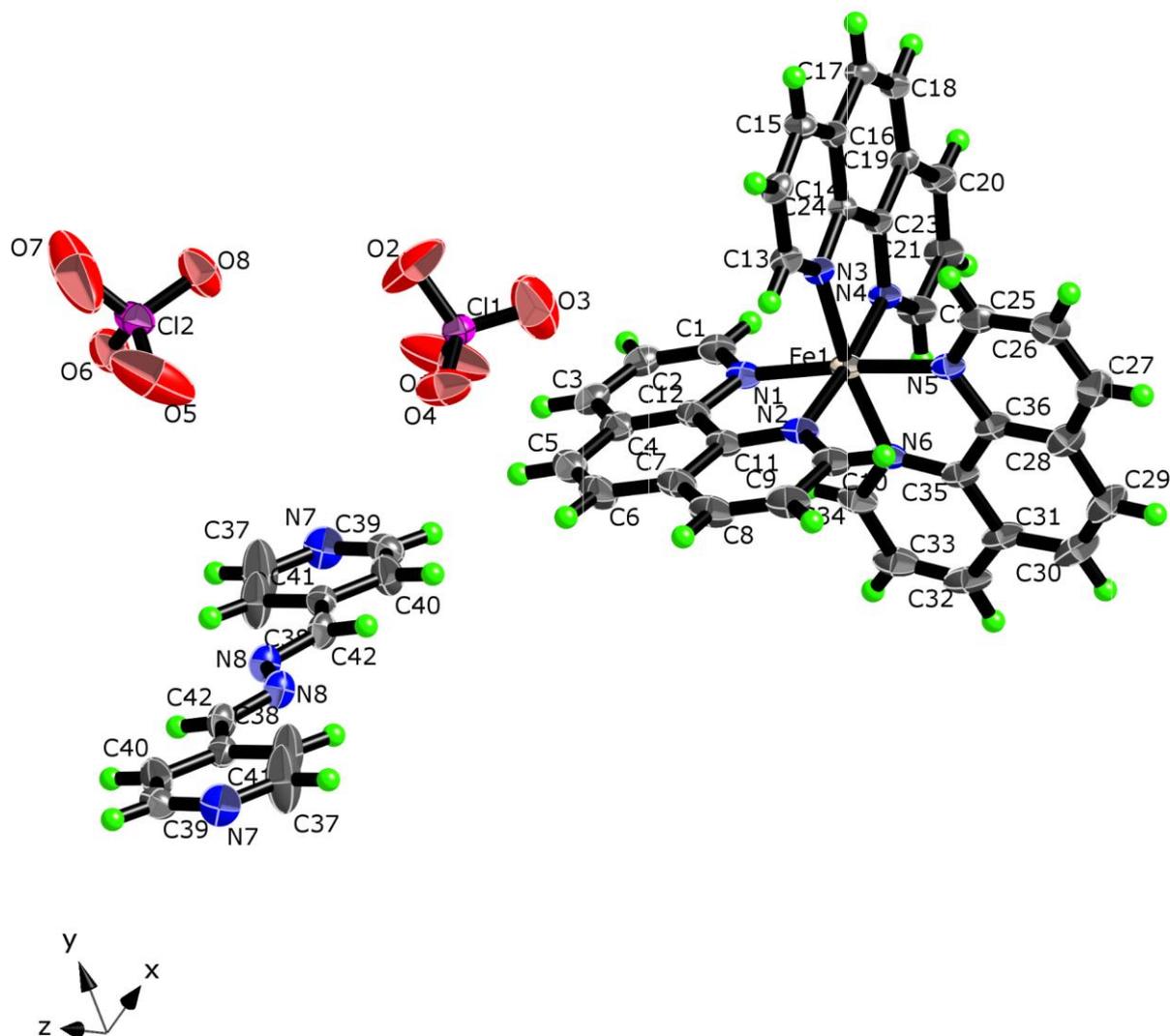


Figure S3. ORTEP type plot and atomic numbering for **2** (In tables S4-S6 the atoms of the 1,2-bis(4-pyridylmethylene)hydrazine unit has been given the suffix “B”).

CSD Searches for many component systems (large values for QUEST “chemical units” parameter)

We got 1750 hits for five components or more (“chemical units” ≥ 5 , a total of 0.4 % of the structures). Many component hits are usually found because of the inclusion of one or more small counter ion, and/or solvent molecules such as water or methanol.

With three or more components, we searched all structures having no individual component having less than 10 carbon atoms, effectively excluding most solvents (also larger ones such a toluene). The 347 hits for the search criteria alone ((“chemical units” ≥ 5 and $nC \geq 10$) were individually inspected to exclude counterions (even larger such as tertiary amines, but not specific molecular ions unless very small) and solvated metal complexes, and moreover retaining only structures having at least three components

distinctively different from a chemical point of view (thus disregarding changes in oxidation state and protonation state).

We found only 55 structures meeting these (somewhat fuzzy) criteria. Of this selection, 19 are calixarenes, a few contain large tetraphenyl type cations, and only three relate in any way to our compound. These are:

1. catena-((m²-4,4'-bipyridyl)-bis(1,3-diphenyl-1,3-propanedionato)-zinc(ii) 4,4'-bipyridine t-butylbenzene clathrate) a 1D coordination polymer with disordered clathrates. (D.V.Soldatov, P.Tinnemans, G.D.Enright, C.I.Ratcliffe, P.R.Diamente, J.A.Ripmeester, *Chem. Mater*, 15, 3826, 2003)
2. catena-(bis(m³-2,4,6-tris(4-Pyridyl)triazine)-tris(di-iodo-zinc) perylene clathrate naphthalene solvate) a 3D coordination polymer with disordered naphthalenes (O.Ohmori, M.Kawano, M.Fujita, *CrystEngComm*, 7, 255, 2005)
3. catena-(4,4'-Bipyridinedi-ium N,N'-dioxide (m²-4,4'-bipyridinedi-ium N,N'-dioxido)-bis(N,N'-bis(salicylidenealdiminato)ethylenediamine)-bis(methanol)-di-manganese(iii)dodecakis(m²-chloro)-bis(m²-cyano)-(m²-4,4'-bipyridinedi-ium N,N'-dioxido)-tetracyano-bis(N,N'-bis(salicylidenealdiminato)ethylenediamine)-di-manganese(iii)-hexa-niobium) a 1D coordination polymer (Jian-Jun Zhang, Yue Zhao, S.A.Gamboa, A.Lachgar, *Cryst Growth. & Des.*, 8, 172, 2008).

Compounds in the Cambridge Crystallography Database, CSD, version 5.3, update February 2009 were searched.^[30]

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