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Multi-component self-assembly of molecule based materials by coordination networks and weak intermolecular synthons

Mohamed Ghazzali[a], Vratislav Langer[b], Krister Larsson[c] and Lars Öhrström[b]*

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The coordination polymer $[Fe(SCN)_2(bis\text{-}4\text{-}pyridylaldazine)_2]_n[Fe(phenanthroline)_3]_{2n}(ClO_4)_{2n}\cdot n bis\text{-}4\text{-}pyridylaldazine\cdot 4nH_2O$ ***1*** *was crystallised from a MeOH/MeCN solution and structure consists of layered (4,4) 2D-nets with supramolecular $([Fe(phen)_3]_2bphz)^{4+}$ units in the pores and disordered water and perchlorate anions. The same supramolecular motif could be independently prepared as $[Fe(phen)_3]_2\cdot bphz(ClO_4)_4xMeOH$* ***2****, and the $[Ru(phenanthroline)_3]^{2+}$ compound* ***3****, isotructural to* ***1****, was also prepared although a complete structure determination was prevented by low crystal quality. Compounds* ***1*** *and* ***3*** *are rare examples of how several large and different components can be assembled inside a 2D coordination network and provides a concept for multi-component self-assembly.*

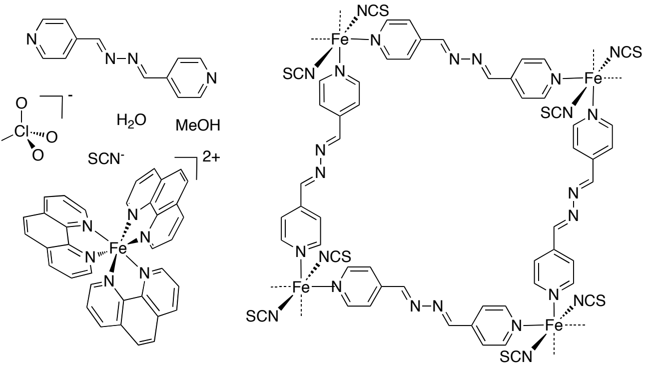
The construction of molecular devices incorporating different functions can be achieved by covalent synthesis. This is an advantage in many cases, and current synthetic methods enable us to build almost any reasonable molecule.[1]

However, the cost of such materials may become forbidding in real applications if a large number of synthetic steps are required. Thus, if the final properties do not depend on covalently linking the parts, it would be advantageous to let a multi-component system self-assemble in a way that creates the desired relation between all the molecules.[2] Here we explore this strategy to create an ordered multi-component system inside a 2D metal-organic framework (MOF).

The obstacle to this solid state self assembly methodology is that although we have a name for this, "crystal engineering",[3] with a few exceptions we do not really know how to do it. Thus, resorcinarenes and related molecules are examples where supramolecular solution chemistry has given some spectacular examples of multi-component self assembly,[4] and also a few materials characterised by X-ray diffraction.[5] With the use of hydrogen bond "synthons", two-component and sometimes even ternary, acid-base systems can be fairly reliably assembled,[6] but without control of the overall crystal structures. The same is true for some very recent examples of multi-component self-assembly inside discrete, crystalline, cage like molecules.[7] Moreover, on surfaces, ternary examples have been reported comprising two-component systems self assembling and then selectively incorporating fullerene molecules.[8]

We can also to some extent control the formation of two- and three-dimensional networks through coordination bonds.[9] In these we can use inclusion of solvents to gain some control over the magnetic properties[10] and it has been shown how carboxylate MOFs with large pores can bind polycyclic molecules and C_{60}.[11] Such networks may also be templated by the presence of larger molecules, usually by excess ligands or solvent. An example is the formation of the chiral $[M(oxalato)_3M']^{n-}$ **srs**-nets[12] by the shape and symmetry complementary $[M''(phen)_3]^{m+}$ cations.[13] More deliberate examples are rotaxane frameworks where circular molecules have been threaded upon a 2D or 3D network.[14]

Presently, however, framework systems such as those described above seem to be restricted to two-component systems (disregarding counter ions and small solvent molecules, and count the network as one component) but in this communication we present a self-assembled three-component system based on a 16×16 Å square-grid Fe(II) coordination polymer. This system is based on the reaction of KSCN, $Fe(ClO_4)_2$, 1,2-bis(4-pyridylmethylene)hydrazine (bphz) and phen, giving $[Fe(SCN)_2(bphz)_2]_n[Fe(phen)_3]_{2n}(ClO_4)_{2n}\cdot n(bphz)\cdot 4nH_2O$, **1**, Scheme 1.¶



Scheme 1. Self-assembly components of **1** (not MeOH) and **2** (not SCN^-): bphz, $[Fe(phen)_3]^{2+}$, perchlorate, SCN^-, water and the 2D grid.

Compound **1** contains a (4,4) grid that forms with high probability from bphz and similar ligands giving 13-16 Å wide squares.[10b, 15] The parallel, neutral, nets are stacked with skewing (67°), and inside the squares are two $[Fe(phen)_3]^{2+}$ cations with bphz molecules neatly intercalated, see Fig.1-2.‡ Also present in the structure are ClO_4^- and H_2O.

From a crystal engineering perspective, the task is now to identify the supramolecular synthons that bind the many components into a crystal. Then, it may be possible to define the possibilities to further modify this $[2D\text{-}net]\cdot[M(phen)_3]_2\cdot[L]$ system.

The ClO_4^- in **1** have no specific interactions with other components, this we conclude as the oxygens are disordered, and the disorder is not possible to model or resolve. (Cl…Fe distances 6-7 Å). Similarly, two out of four H_2O are disordered but form hydrogen bonds to each other and to the SCN^-. π-π and σ-π interactions define the position of $[Fe(phen)_3]^{2+}$ relative to the bphz grid.

The relation between the guest molecules in **1** is also defined by π-π and σ-π interactions, and as the bphz is intercalated this creates the supramolecular unit $[Fe(phen)_3]_2bphz^{4+}$, see Fig. 3, left. These units are aligned along the *b*-axis but with no π-stacking as the second Fe2…Fe2 distance is quite long, see Fig. 2

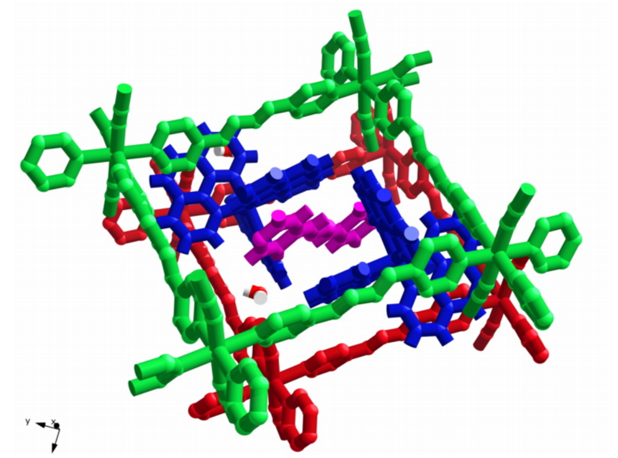


Figure 1. Structure of $[Fe(SCN)_2(bphz)_2]_n[Fe(phen)_3]_{2n}(ClO_4)_{2n}\cdot$ n(bphz) $\cdot 4nH_2O$, **1,** emphasising the squares in the 2D nets and the relation between these, the $[Fe(phen)_3]^{2+}$ cations and the bphz (1,2-bis(4-pyridylmethylene)hydrazine). ClO_4^-, and framework hydrogens have been omitted for clarity.

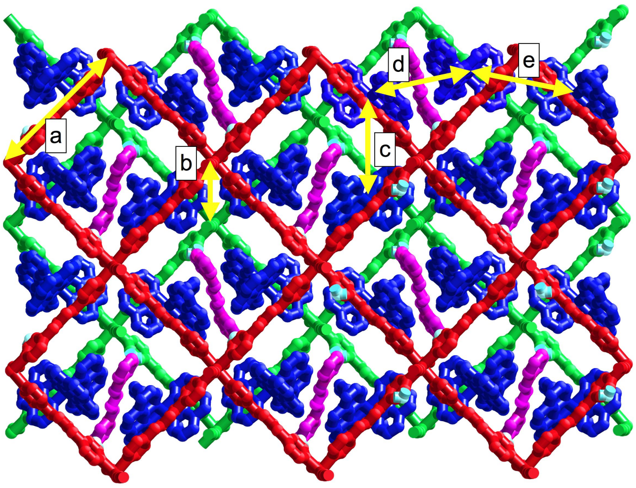


Figure 2. Complete structure of **1**, $[Fe(SCN)_2(bphz)_2]_n[Fe(phen)_3]_{2n}(ClO_4)_{2n}\cdot n(bphz)\cdot 4nH_2O$ with same colour coding as Fig.1 and ClO_4^- and H atoms omitted (except for water, light blue). Pertinent dimensions of the structure (symmetry codes are given in the ESI): Fe1…Fe1: a 15.72 Å; b 13.21 Å, Fe2…Fe2: c 11.22 Å; c 10.60 Å; e 12.09 Å

The inclusion structure is thus dependent on the interactions between the π-systems. Although these are well recognized in the solid state,[16] they are difficult to use in crystal engineering. We therefore need to investigate if this supramolecular synthon can be found also in other structures.

For that reason we also prepared $[Fe(phen)_3]_2\cdot bphz(ClO_4)_4\cdot xMeOH$ **2**, containing bphz units intercalated between $[Fe(phen)_3]^{2+}$ cations in a similar way to **1**, see Fig. 3 right. The bphz also forms a similar compound with $[Cu(dimethyl\text{-}phenanthroline)_2]^+$,[17] but among the 209 structures reported in the Cambridge Crystallographic Database (CSD)[18] containing a $[M(phen)_3]^{n+}$ cation, there are only two other examples of a large flat neutral molecule intercalated between two complexes: $[M(phen)_3]_2(phen)(V_4O_{12})$ (M=Co, Ni).[19]

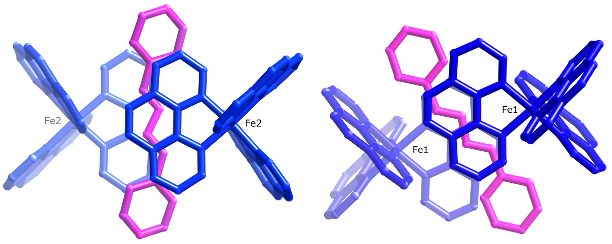


Figure 3. left: $([Fe(phen)_3]_2bphz)^{4+}$ inside the network of **1**, Fe2…Fe2 10.60 Å. Right: the $([Fe(phen)_3]_2bphz)^{4+}$ in $([Fe(phen)_3]_2$ $bphz)(ClO_4)_4\cdot xMeOH$, **2**, Fe1…Fe1 10.34 Å

From inspection of Fig. 3 it is clear that the bphz interactions with the phenanthroline complexes in **1** and **2** have similarities, but it is also clear that the molecular arrangements are not identical, and we can identify at least 16 relevant atom-atom distances that we need to evaluate and compare. This is tedious and hard to do in a consistent manner, and instead Hirshfeld surfaces[20] as implemented in the CrystalExplorer program[21] was used to investigated this.

In this approach a surface is generated that encompasses regions where the electron density (modelled by spherical atoms) from the molecule is dominant over the electron density contributions form the rest of the crystal. At each point of this surface one can map the distances to the closest atom on the inside (d_i) and outside (d_e) of the surface, generating plots where, for example, weak hydrogen bonds are easily detected.

In a mathematically less transparent operation the properties of the Hirshfeld surface itself, such as the curvature, can be mapped, and it has been suggested that the most informative way to look at π-π interactions is the *shape index*.[20a] This number, *S*, is based on the sum of the two principal curvatures of the surface, κ_1 and κ_2, divided by the their differences:

$$S = (2/\pi) \arctan [(\kappa_1 + \kappa_2)/(\kappa_1 - \kappa_2)] \qquad (1)$$

The *shape index* "is a dimensionless measure of 'which' shape"[20a], and for areas where the shape index have different signs, displayed as red or blue areas in Fig. 4, we expect the adjoining molecules to have a complementary pattern.

For **1** and **2** the shape index mapping has been plotted for the bphz grid and inclusion molecules, see Fig. 4. Clearly the inclusion molecules (centre and bottom) have related characteristics for the central C=N-N=C part, for example the blue areas running across the waist of the molecules are similar. For the Fe-bphz-Fe link these band are clearly absent. Comparing the more peripheral parts of the molecules is not possible as the squeeze procedure used in the crystallographic refinement and the disorder in the crystals will produce artefacts.

It should also be noted that the Hirshfeld surface approach is relatively new and when used in work such as the present communication, this means that not only the crystals structures themselves are investigated; we are also evaluating the usefulness of the method.

These interactions are perhaps not simple π-π stackings as the phenanthroline has donor properties and the C=N bonds some acceptor character. We therefore compared benzene fragments having close interactions of a CC unit to a C=N-N=C or C=CH-CH=C fragment in the CSD. Of the 160 hits of the first type, 35% had C…(C or N) contacts < 3.8 Å and 19% had also the benzene and C=N-N=C mean planes parallel ($\alpha<10°$). The values for the corresponding C=CH-CH=C interactions were 9.5% and 6%.

An attractive extension of this approach to self-assembly would be to incorporate different metal ions in the intercalation compound and in the framework. As a proof of concept we therefore prepared the $[Ru(phen)_3]^{2+}$ analogue to **1**, i.e. compound **3**. Although quality problems with these crystals prevented a complete structure determination, the identical space group, and the near identical cell parameters, (a small increase in volume consistent with the slightly larger Ru^{2+} ion was observed) lead to the conclusion that **1** and **3** are isostructural.

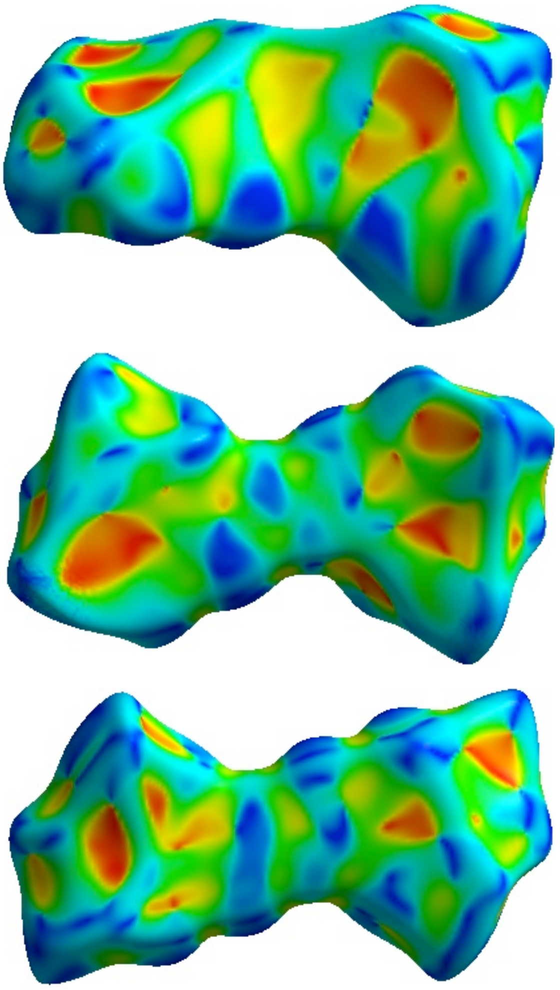


Figure 4. The *shape index*, as implemented in the CrystalExplorer program,[21] showing regions of π–π stacking for a bphz link in **1** (top), and for the inclusion molecules in **1** (middle) and **2** (bottom)**.** Shape index, *S*, (eq. 1) mapped from concave; red, over minimal saddle; green, to convex; blue.

The occurrence of both Δ and Λ $[M(phen)_3]^{2+}$ in the structure also suggests the possibility of introducing two different complex ions by the use of the pure Δ or Λ forms. Moreover, given the many MOFs published to-date, there is ample choice to test this concept on other framework types. As noted elsewhere, these nets may be a tool for exact positioning of molecular components in the solid state,[9d] and one of the original ideas of the term MOF was that these "frames" could be used to "hang" molecules on.[22]

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,[23] or other combinations of the molecular entities present. [24]

Tris(1,10-phenanthroline)iron(II)chloride,[25] tris(1,10-phenanthroline) iron(II)perchlorate hydrate,[25] tris(1,10-phenanthroline)ruthenium(II) chloride[26] and 1,2-bis(4-pyridylmethylene)hydrazine[27] were prepared, with minor modifications, according to the literature.

***$[Fe(SCN)_2(\text{bis-4-pyridylaldazine})_2]_n[Fe(\text{phenanthroline})_3]_{2n}\ (ClO_4)_{2n}\cdot n\text{bis-4-pyridylaldazine}\cdot 4nH_2O$* 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 N_2 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 $KClO_4$ could not be avoided IR: (γ, cm^{-1}, KBr): 501(m) [$\upsilon_{M\text{-}N}$], 624(m) [SCN^-], 730(m)[SCN^-], 849(m)[SCN^-], 1090(s)[ClO_4^-], 1427(s)[$\delta_{C=N}$], 3524(s) [$H_2O_{\text{stretching}}$]. Analytical data for $C_{110}H_{90}Cl_{4.85}Fe_3K_{0.85}N_{26}O_{25.4}S_2$: Calc.: C, 50.44; H, 3.46; N, 13.91. Found: C, 50.80; H, 2.90; N, 13.90.

$[Fe(phen)_3]_2\cdot bphz(ClO_4)_4\cdot xMeOH$ 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 ($[Fe(phen)_3]_2bphz(ClO_4)_4\cdot nMeOH$) **2** were collected and dried in air. IR: (γ, cm^{-1}, KBr): 509(m)[$\upsilon_{M\text{-}N}$], 624(m)[C=C], 1085(s)[ClO_4^-], 1425(s) [$\delta_{C=N}$].

***$[Fe(SCN)_2(\text{bis-4-pyridylaldazine})_2]_n[Ru(\text{phenanthroline})_3]_{2n}\ (ClO_4)_{2n}\cdot n\text{bis-4-pyridylaldazine}\cdot 4nH_2O$* 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 N_2 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) [$\upsilon_{M\text{-}N}$], 742(m)[SCN^-], 1150(s)[ClO_4^-], 1405(s)[$\delta_{C=N}$],.

X-ray diffraction Diffraction data for **1-3** were collected using a Siemens SMART CCD diffractometer with Mo-Ka radiation (λ=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.[28] 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 > 10σ (I) after integration of all the frames using SAINT[29]. 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 ClO_4^- as well as one disordered H_2O molecules in 1 and two disordered ClO_4^- as well as one disordered MeOH molecule in 2 could not be modelled properly and were squeezed out with PLATON[30]. Thermal displacement plots are given in Figures 5 and 6.

1 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, α=γ=90°, β=93.242(1)°, V=5483.3(4) $Å^3$, θ range=2.05-25.26°, Completeness to θ_{max} =99.5 %, Data/restraints/parameters: 9889/2/652, Measured refl., 60159, Unique refl., 9889, R_{int}=0.0627, R(I>2σ)=0.0480, wR_2(all)=0.1472, S=1.004, Largest peak/hole: 0.587 /-0.269 e.$Å^{-3}$ CCDC: 758946.

2 Formula: $C_{42.5}H_{31}Cl_2FeN_8O_{8.5}$, Mr=916.50, Z=2, Triclinic, Space group P-1 (no.2), a=12.2473(4), b=12.6914(5), c=13.7110(5) Å, α=79.294(1), β=74.263(1), γ=69.511(1)°, V=1911.75(12) $Å^3$, θ range=2.07-30.00°, Completeness to θ_{max}=99.7 %, Data/restraints/parameters: 11108/0/460, Measured refl. 30745, Unique refl., 11108, R_{int}=0.035, R(I>2σ)=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, α=γ=90°, β=94.393(9)°, V=5502.734(4) $Å^3$. Complete refinement not possible due to low crystal quality.

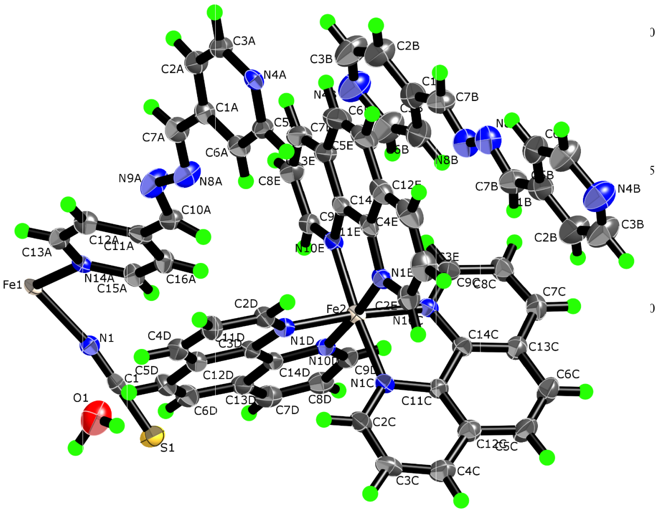


Figure 5. A displacement ellipsoid plot of **1** (content of the asymmetric unit) at 50% level.

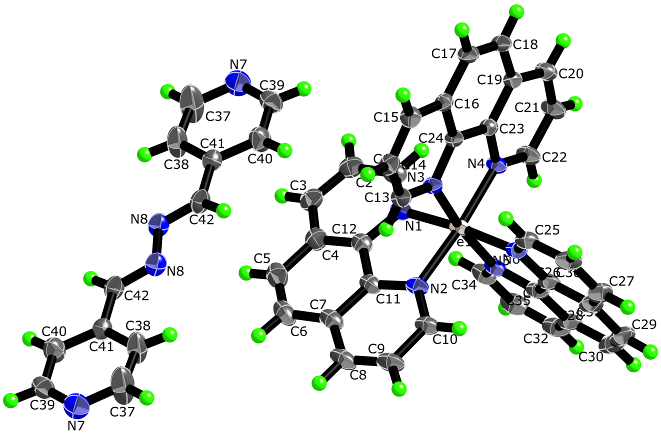


Figure 6. A displacement ellipsoid plot of **2** (content of the asymmetric unit) at 50% level.

CSD Searches for many component systems

Searching the Cambridge Crystallography Database, CSD, version 5.3, update February 2009[33] 1750 hits were recorded having five components or more (“chemical units” ≥ 5, a total of 0.4 % of the structures in the database). We noted that 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 with 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” ≥ 3 and nC ≥ 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 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 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-butyl-benzene clathrate) a 1D coordination polymer with disordered chlathrates.[34]

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 naphtalenes.[35]

3.Catena-(4,4'-Bipyridinedi-ium N,N'-dioxide (m2-4,4'-bipyridinedi-iumN,N'-dioxido)-bis(N,N'-bis(salicylidene aldiminato) ethylene diamine)-bis(methanol)-di-manganese(iii) dodecakis(m2-chloro)-bis(m2-cyano)-(m2-4,4'-bipyridinedi-ium N,N'-dioxido)-tetra cyano-bis(N,N'-bis(salicylidenealdiminato) ethylenediamine)-di-manganese(iii)-hexa-niobium) a 1D coordination polymer.[36]

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Notes and references

[a] *Address, Chemistry Department, King Saud University, PO Box 2455 Riyadh 11451, Kingdom of Saudi Arabia*
[b] *Address, Department of Chemical and Biological Engineering, Chalmers Tekniska Högskola, SE 412 96, Gothenburg, Sweden*
[c] *Address, MaxLab, Lund University, SE-22100 Lund, Sweden*

† Electronic Supplementary Information (ESI) available: Experimental and structural details for **1**-**3**. See DOI: 10.1039/b000000x/

1. (a) K. C. Nicolaou and S. A. Snyder, *Classics in total synthesis II: more targets, strategies, methods*, VCH, Weinheim, 2003,(b) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd edn., Pergamon Press, Oxford, 1997.
2. M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910-1921.
3. (a) M. J. Zaworotko, *Cryst. Growth Des.*, 2007, **7**, 4-9, (b) D. Braga, L. Brammer and N. R. Champness, *Crystengcomm*, 2005, **7**, 1-19,(c) P. Erk, R. van Gelder, M. F. Haddowand and H. Hengelsberg, *Crystengcomm*, 2004, **6**, 474 - 483,(d) L. Brammer, *Chem. Soc. Rev.*, 2004, **33**, 476-489,(e) D. Braga, *Chem. Commun.*, 2003, 2751,(f) D. Braga, G. Desiraju, J. Miller, A. Orpen and S. Price, *Crystengcomm*, 2002, 500.
4. A. Scarso, A. Shivanyuk and J. Rebek, *J. Am. Chem. Soc.*, 2003, **125**, 13981-13983.
5. (a) C. L. Barnes and E. Bosch, *Cryst. Growth Des.*, 2005, **5**, 1049-1053,(b) B. Q. Ma, L. F. V. Ferreira and P. Coppens, *Org. Lett.*, 2004, **6**, 1087-1090,(c) L. R. MacGillivray, P. R. Diamente, J. L. Reid and J. A. Ripmeester, *Chem. Commun.*, 2000, 359-360,(d) C. L. Raston and G. W. V. Cave, *Chem. Eur. J.*, 2004, **10**, 279-282.
6. C. B. Aakeroy, J. Desper and M. M. Smith, *Chem. Commun.*, 2007, 3936-3938.
7. (a) S. Horiuchi, Y. Nishioka, T. Murase and M. Fujita, *Chem. Commun.*, 2010, **46**, 3460-3462,(b) I. Imaz, J. Hernando, D. Ruiz-Molina and D. Maspoch, *Angew. Chem. Int. Ed.*, 2009, **48**, 2325-2329,(c) T. Murase, K. Otsuka and M. Fujita, *J. Am. Chem. Soc.*, 2010, **132**, 7864-+.
8. J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature*, 2003, **424**, 1029-1031.
9. (a) R. Robson, *Dalton Trans.*, 2000, 3735-3744,(b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705-714, (c) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176-182,(d) L. Öhrström and K. Larsson, *Molecule-Based Materials: The Structural Network Approach*, Elsevier, Amsterdam, 2005,(e) S. R. Batten, *J. Solid State Chem.*, 2005, **178**, 2475-2479.
10. (a) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nature Materials*, 2003, **2**, 190-195,(b) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762-1765.
11. H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2004, **427**, 523-527.
12. M. O'Keeffe, O. M. Yaghi and S. Ramsden, *Reticular Chemistry Structure Resource*, Australian National University Supercompuer Facility, http://rcsr.anu.edu.au/ Accessed April 2011
13. S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling and P. Gütlich, *J. Am. Chem. Soc.*, 1994, **116**, 9521.
14. (a) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247-289,(b) E. S. Lee, J. S. Heo and K. Kim, *Angew. Chem. Int. Ed.*, 2000, **39**, 2699-2701,(c) D. J. Hoffart and S. J. Loeb, *Angew. Chem. Int. Ed.*, 2005, **44**, 901-904,(d) Q. W. Li, W. Y. Zhang, O. S. Miljanic, C. H. Sue, Y. L. Zhao, L. H. Liu, C. B. Knobler, J. F. Stoddart and O. M. Yaghi, *Science*, 2009, **325**, 855-859.
15. M. Du, Y.-M. Guo, S.-T. Chen, X.-H. Bu, S.R.Batten, J.Ribas and S.Kitagawa, *Inorg.Chem.*, 2004, **43**, 1287-1293.
16. (a) I. Dance and M. Scudder, *J. Chem. Soc., Chem. Commun.*, 1995, 1039-1040,(b) C. Janiak, *Dalton Trans.*, 2003, 2781-2804.
17. G. King, M. Gembicky and P. Coppens, *Acta Crystallogr.,Sect.C.*, 2005, **61**, m329.
18. F. H. Allen, *Acta Cryst. B.* 2002, **58**, 380-388.
19. L. Zurkova, R. Kucsera, R. Gyepes and M. Sivak, *Monatsh. Chem.*, 2003, **134**, 1071-1079.
20. (a) J. J. McKinnon, M. A. Spackman and A. S. Mitchell, *Acta Cryst. B.*, 2004, **60**, 627-668,(b) M. A. Spackman and D. Jayatilaka, *Crystengcomm*, 2009, **11**, 19-32,(c) M. A. Spackman and J. J. McKinnon, *Crystengcomm*, 2002, 378-392.
21. S. K. Wolff, D. J. Grimwood, J. J. McKinnon, D. Jayatilaka and M. A. Spackman, Univ. of Western Australia, Perth, Australia, 2007.
22. M. O'Keeffe, personal communication, 2009.
23. M. Ghazzali, V. Langer, L. Öhrström and M. A. M. Abu-Youssef, *Acta Cryst.*, 2007, **C63**, o312-0314.
24. (a) M. Ghazzali, V. Langer and L. Öhrström, *J. Solid State Chem.*, 2008, **181**, 2191-2198,(b) M. Ghazzali, L. Öhrström, P. Lincoln and V. Langer, *Acta Cryst. C.*, 2008, **64**, M243-M245,(c) L. Öhrström, V. Langer and M. Ghazzali, *Acta Cryst. C.*, 2008, **64**, M277-M279.
25. D. Nicholls, *The Chemistry of Iron, Cobalt and Nickel, Vol. 24*, Pergamon Press, Oxford, **1975**.
26. P. Lincoln, B. Norden, *J. Phys. Chem. B* **1998**, *102*, 9583-9594.
27. N. R. Elrayyes, A. H. Katrib, *J. Chem. Eng. Data* **1983**, *28*, 132-134.
28. SMART, Bruker AXS Inc., Madison, Wisconsin, USA., **2003**.
29. SAINT, Bruker AXS Inc., Madison, Wisconsin, USA., **2003**.
30. SADABS, G. M. Sheldrick, University of Göttingen, Germany, **2003**.
31. SHELXL, Bruker AXS Inc. , Madison, Wisconsin, USA., **2003**.
32. A. L. Spek, Utrecht University, Padualaan 8, 3584 CH, Utrecht, the Netherlands., **2005**.
33. F. H. Allen, W. D. S. Motherwell, *Acta Cryst. B* **2002**, *58*, 407-422.
34. D.V.Soldatov, P.Tinnemans, G.D.Enright, C.I.Ratcliffe, P.R.Diamente, J.A.Ripmeester, *Chem. Mater*, 15, 3826, **2003**
35. O.Ohmori, M.Kawano, M.Fujita, *CrystEngComm*, 7, 255, **2005**
36. Jian-Jun Zhang, Yue Zhao, S.A.Gamboa, A.Lachgar, *Cryst Growth. & Des.*, 8, 172, **2008**