ELECTRONIC SUPPORTING INFORMATION

Water structures and packing efficiency in methylene blue cyanometallate salts

Stefano Canossa,[1, *] Claudia Graiff,[2, *] Domenico Crocco,[2] and Giovanni Predieri[2]

[1] EMAT, Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium.

[2] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università degli Studi di Parma, Via Parco Area delle Scienze 17/A, 43124 Parma, Italy.

* Corresponding authors: stefano.canossa@uantwerpen.be; claudia.graiff@unipr.it

1. Single-crystal X-ray diffraction

1.1. Additional refinement details

1.1.1. Compound **1** (MB$_2$[Ni(CN)$_4$]·2H$_2$O)

Due to poor data quality, only the location of the two oxygen atoms of the water molecules, but not their hydrogen atoms, has been determined. Due to displacive disorder of one of the two water molecules (upper one in figure S1), further enhanced by the temperature conditions (298K), the hydrogens were fixed at a certain distance and geometry to the nitrogen atoms of the methylene blue.

Although this forces the interaction discussed in the main text, this solution only ensured a converging refinement and a chemically sound structure, in agreement with the available evidence in the literature. Due to this modelling choices, the exact refined value of the hydrogen bonding distance of this specific water molecule towards the aromatic nitrogen and the second water molecule should not be considered derived from experimental observations.
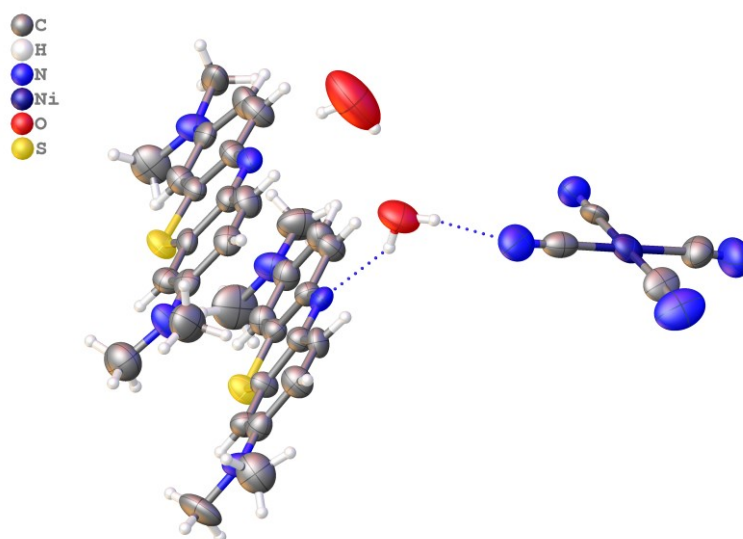

Figure S1. Refined asymmetric unit of compound **1.**

1.1.2. Compound **2** (MB$_2$[Fe(CN)$_5$NO])

The highly overlapping CN and NO groups were refined by restraining their internal and coordination bond distances according to values taken from the literature.

A representative structural model was found in a structure deposited in the Cambridge Structural Database with reference code "HADZAO01". Here, Fe-CN coordination distances range from 1.933 Å to 1.945 Å, while for Fe-NO the distance is 1.645 Å.

In the asymmetric unit of compound **2**, three independent ligands are present. For two of them two types of coordination bond distances can be recognised from the electron density maxima,

one at approximate distance of 1.94 Å and one at 1.70 Å, which can be considered an average position between the CN and NO group. Coordination distances have been therefore restrained to 1.94 Å and 1.65 Å for CN and NO respectively. Internal CN and NO bonds were restrained to 1.15 Å resulting in bond distances ranging from 1.135 Å and 1.150 Å. Restraints for ADPs belonging to CN and NO were used to ensure reasonable displacement parameters (RIGU and ISOR).
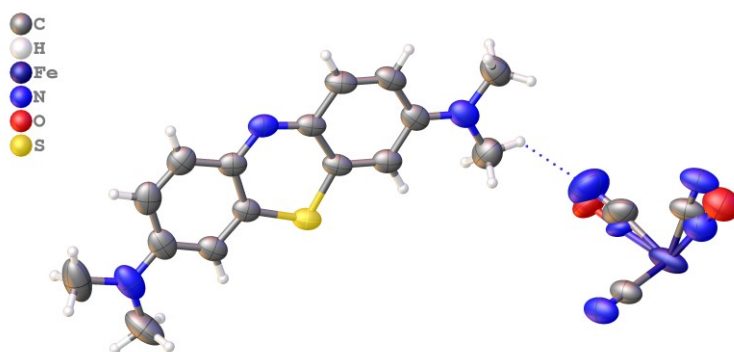

Figure S2. Refined asymmetric unit of compound **2.**

1.1.3. Compound **3** (MB$_3$[Fe(CN)$_6$]·H$_2$O)

As the disordered MB molecule sits on an inversion centre, the two conformations are strongly overlapped. Thus, all atomic positions, found as electron density peaks for non-hydrogen atoms, were subjected to suitable restraints/constraints (DFIX, DANG and AFIX66) to guarantee a final chemically sound structure and assist the refinement towards convergence.
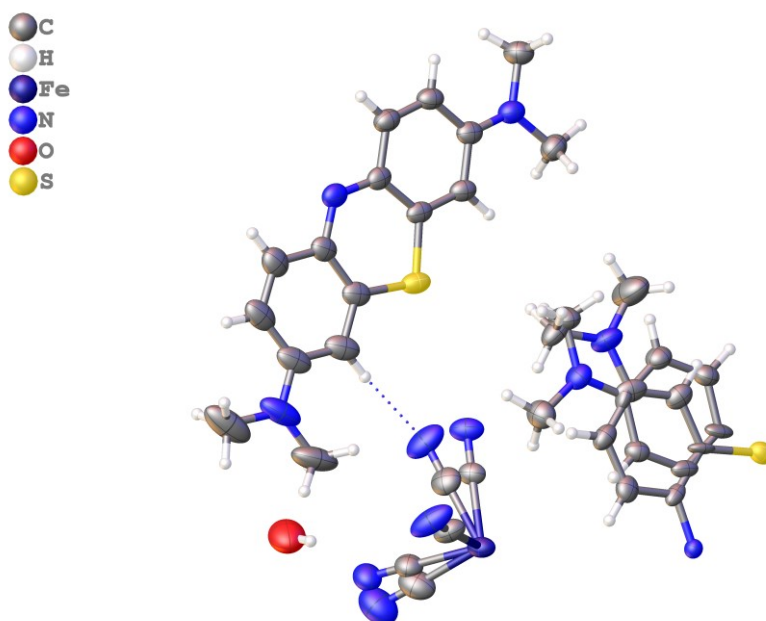

Figure S3. Refined asymmetric unit of compound **3.**

1.1.4. Compound 4 (MB$_3$[Fe(CN)$_6$]·12.36H$_2$O)

A structure solution in using a P-1 space group has also been attempted, although resulting in an asymmetric unit with an ordered and a disordered MB molecule, which has not been possible to model satisfactorily. After including an inversion twinning, the structure solution in P1 resulted to be the one affording the most reliable and high-quality crystallographic structure.

As can be seen from Figure S4, some water molecules have more than 2 hydrogen atoms. This is due to an identified positional disorder of these hydrogens, which have been located in the difference Fourier maps, fixed to the oxygen atoms they are connected to, and refined considering the sum of the disordered parts occupancies to be 1.
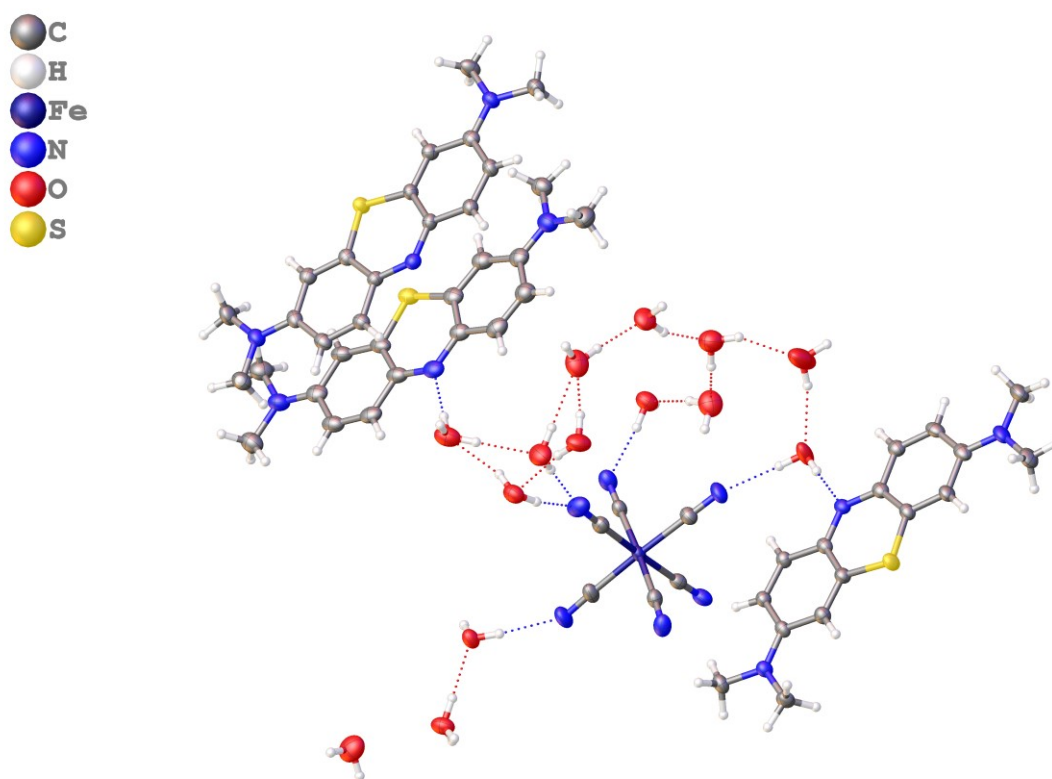

Figure S4. Refined asymmetric unit of compound **4.**

1.2 Crystallographic information tables

Table S1. Crystallographic details for compound **1**

Empirical form.	$C_{36}H_{40}N_{10}NiO_2S_2$	μ/mm^{-1}	0.695
Form. weight	767.61	F(000)	1608.0
Temp./K	298	Crystal size/mm^3	0.3 × 0.05 × 0.05
Crystal system	Monoclinic	Radiation	MoKα (λ = 0.71073)
Space group	Cc	2Θ range for data collection/°	3.528 to 41.626
a/Å	16.58(3)	Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -13 ≤ l ≤ 13
b/Å	16.19(3)	Reflections collected	9574
c/Å	13.68(2)	Independent reflections	3766 [R_{int} = 0.1643, R_{sigma} = 0.2169]
α/°	90	Data/restraints/parameters	3766/239/476
β/°	96.94(3)	Goodness-of-fit on F^2	0.960
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0740, wR_2 = 0.1284
Volume/Å^3	3646(11)	Final R indexes [all data]	R_1 = 0.1700, wR_2 = 0.1662
Z	4	Largest diff. peak/hole / e Å^{-3}	0.28/-0.38
ϱ_{calc} g/cm^3	1.398	Flack parameter	0.22(8)
			(twin law: -1 0 0 0 1 0 0 0 -1)

Table S2. Crystallographic details for compound **2**

Empirical form.	$C_{37}H_{36}FeN_{12}OS_2$	μ/mm^{-1}	0.565
Form. weight	784.75	F(000)	816.0
Temp./K	100	Crystal size/mm^3	0.06 × 0.015 × 0.015
Crystal system	Monoclinic	Radiation	Synchrotron (λ = 0.700)
Space group	P2$_1$/n	2Θ range for data collection/°	5.322 to 54.84
a/Å	7.9790(2)	Index ranges	-10 ≤ h ≤ 10, -19 ≤ k ≤ 19, -19 ≤ l ≤ 19
b/Å	15.0782(2)	Reflections collected	25176
c/Å	15.1639(2)	Independent reflections	4163 [R_{int} = 0.0453, R_{sigma} = 0.0268]
α/°	90	Data/restraints/parameters	4163/180/282
β/°	100.228(2)	Goodness-of-fit on F^2	1.040
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0706, wR_2 = 0.1960
Volume/Å^3	1795.36(6)	Final R indexes [all data]	R_1 = 0.0794, wR_2 = 0.2060
Z	2	Largest diff. peak/hole / e Å^{-3}	1.01/-0.86
ϱ_{calc} g/cm^3	1.452		

Table S3. Crystallographic details for compound **3**

Empirical form.	$C_{54}H_{56}FeN_{15}OS_3$	μ/mm^{-1}	0.469
Form. weight	1083.16	F(000)	1134.0
Temp./K	100	Crystal size/mm^3	0.08 × 0.02 × 0.02
Crystal system	Monoclinic	Radiation	Synchrotron (λ = 0.700)
Space group	P2$_1$/n	2Θ range for data collection/°	3.75 to 54.842
a/Å	10.8838(4)	Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -20 ≤ l ≤ 20
b/Å	15.2399(5)	Reflections collected	36185
c/Å	15.4106(6)	Independent reflections	5924 [R_{int} = 0.0542, R_{sigma} = 0.0384]
α/°	90	Data/restraints/parameters	5924/135/456
β/°	102.913(4)	Goodness-of-fit on F^2	1.056
γ/°	90	Final R indexes [I>=2σ (I)]	R$_1$ = 0.0790, wR$_2$ = 0.2034
Volume/Å^3	2491.48(16)	Final R indexes [all data]	R$_1$ = 0.0958, wR$_2$ = 0.2146
Z	2	Largest diff. peak/hole / e Å^{-3}	0.98/-1.29
ϱ_{calc} g/cm^3	1.444		

Table S4. Crystallographic details for compound **4**

Empirical form.	$C_{54}H_{78.7}FeN_{15}O_{12.35}S_3$	μ/mm^{-1}	0.404
Form. weight	1287.83	F(000)	681.0
Temp./K	100	Crystal size/mm^3	0.06 × 0.05 × 0.04
Crystal system	Triclinic	Radiation	Synchrotron (λ = 0.700)
Space group	P1	2Θ range for data collection/°	3.106 to 51.888
a/Å	9.7710(19)	Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -17 ≤ l ≤ 15
b/Å	12.201(2)	Reflections collected	18710
c/Å	13.651(3)	Independent reflections	10608 [R_{int} = 0.0285, R_{sigma} = 0.0445]
α/°	84.18(3)	Data/restraints/parameters	10607/22/849
β/°	72.06(3)	Goodness-of-fit on F^2	1.053
γ/°	89.45(3)	Final R indexes [I>=2σ (I)]	R$_1$ = 0.0439, wR$_2$ = 0.1199
Volume/Å^3	1539.9(6)	Final R indexes [all data]	R$_1$ = 0.0442, wR$_2$ = 0.1202
Z	1	Largest diff. peak/hole / e Å^{-3}	0.63/-0.68
ϱ_{calc} g/cm^3	1.389	Flack parameter	0.376(14)
			(twin law: -1 0 0 0 1 0 0 0 -1)

1.3. Reciprocal space reconstructions
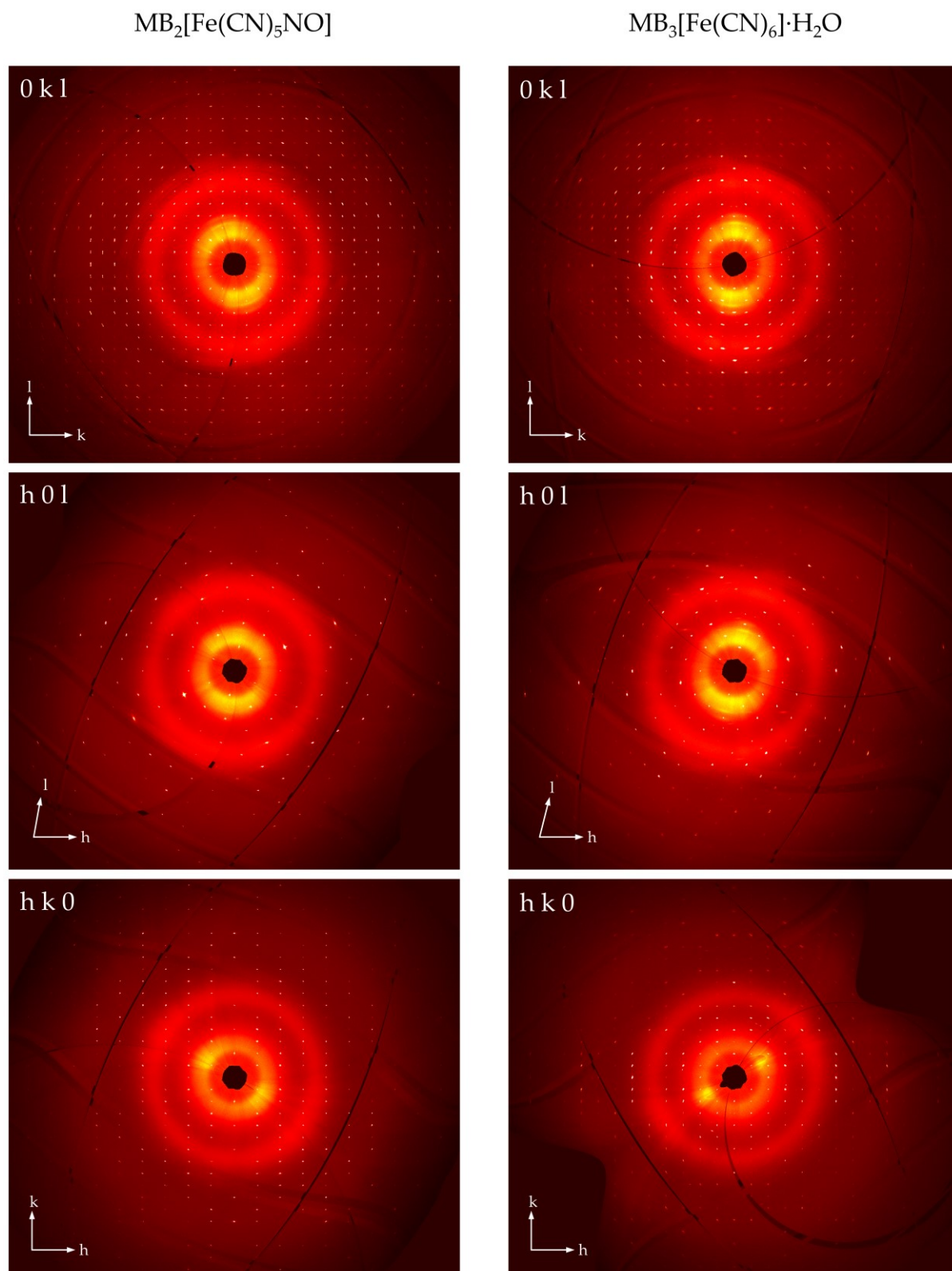
MB$_2$[Fe(CN)$_5$NO]   MB$_3$[Fe(CN)$_6$]·H$_2$O

Figure S5. Reciprocal space reconstructions for compound **2** and **3**, affected by structural disorder. As can be inferred by the reconstructions, the observed is poorly correlated and diffuse scattering attributable to disorder is hardly distinguishable. The Bragg reflections seem relatively sharp, except for a slight concentric elongation due to mosaic spread in the crystals.

2. Structural graphics

The figures shown in the main text were obtained by using the software Mercury of the Cambridge Structural Database System and the crystallographic visualisation software Vesta; the references for both programs are given in the main text.

In particular, the display of the voids allocating the water molecules in compound **4** was made by using the "Display voids" function of Mercury after manually removing the water molecules from the cif file. For this calculation, a probe radius of 1.2 Å, grid spacing 0.3 Å and the "contact surface" mode have been used.

The coloured Hirshfeld regions displayed with characteristic colours shown in Figures 6-9 were created using Microsoft Power Point 2016.

The original Hirshfeld fingerprint plots have been exported by the Crystal Explorer program and edited in Power Point 2016 during the preparation of the final pictures.