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Supplementary Information

Structural and magnetic characterization of Ni(II), Co(II), Fe(II) binuclear complexes on bispyridyltriazolylalkanes basis.

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Table S1. Crystal data and structure refinements for the reported compounds.

Parameter/Complex	**1a**	**1b**	**2b**	**3a**	**3b**
Formula	$C_{16}H_{22}N_{10}NiO_{10}$	$C_{16}H_{18}CoN_{10}O_8$	$C_{34}H_{44}Co_2N_{20}O_{13}$	$C_{36}H_{48}N_{20}Ni_2O_{18}$	$C_{72}H_{114}Co_4N_{40}O_{45}$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P 2_1/c	I2/c	P 2_1/n	P 2_1/c	P nna
a, Å	8.1311(6)	15.2228(6)	12.1261(8)	12.203(2)	16.1207(19)
b, Å	27.5357(19)	10.2158(4)	31.410(2)	29.025(6)	42.286(5)
c, Å	10.5281(7)	14.4221(5)	13.6475(10)	15.894(3)	15.3893(18)
α °					
β°	102.1120(10)	110.266(4)	109.6370(10)	107.88(3)	
γ°					
V, Å ^{3}	2304.7(3)	2103.98(15)	4895.8(6)	5358(2)	10491(2)
Z	4	4	4	4	4
μ_{Mo}. mm^{-1}	0.918	0.886	0.753	0.788	0.732
Parameters	356	167	645	697	790
Number of symmetry-independent reflections/ Number of reflections with I > 2σ(I)	5035/3670	2413 / 2175	8617/7194	9439/6088	11468/8656
R(I > 2σ(I))	0.0429	0.0324	0.0519	0.0601	0.0707
w*R*$_2$	0.0919	0.0745	0.1309	0.1530	0.1636
Parameter/Complex	**4a**	**4c**	**5a**	**5b**	**5c**
Formula	$C_{36}H_{32}Cl_2N_{16}Ni_2O_{12}$	$C_{36}H_{32}B_2F_8Fe_2N_{16}O_4$	$C_{44}H_{56}Cl_2N_{16}Ni_2O_{18}$	$C_{44}H_{56}B_2Co_2F_8N_{16}O_{10}$	$C_{44}H_{56}B_2F_8Fe_2N_{16}O_{10}$
Crystal system	monoclinic	monoclinic	monoclynic	monoclynic	monoclynic
Space group	P 2_1/c	P 2_1/c	P 2_1/c	P 2_1/c	P 2_1/c
a, Å	12.3683(3)	12.445(5)	14.649(5)	14.538(5)	14.527(5)
b, Å	15.2467(3)	15.122(5)	12.745(5)	12.883(5)	12.915(5)
c, Å	16.1543(4)	16.263(5)	17.960(4)	18.054(4)	18.114(4)
β°	128.416(2)	128.124(19)	125.061(18)	125.500(18)	125.778(18)
V, Å ^{3}	2386.84(11)	2407.7(15)	2744.7(16)	2752.8(16)	2757.1(16)
Z	2	2	2	2	2
μ_{Mo}. mm^{-1}	0.975	0.688	0.870	0.699	0.623
Parameters	303	307	384	397	397
Number of symmetry-independent reflections/ Number of reflections with I > 2σ(I)	4180/3241	4239/3174	4380/3236	4835/4106	4846/3826
R(I > 2σ(I))	0.0517	0.0551	0.0474	0.0278	0.0342
w*R*$_2$	0.1502	0.1562	0.1225	0.0730	0.0856

Table S2. Selected bond’s length for the reported compounds

1a		**1b**		**2b**				**3a**			
Bond	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**
Ni1-N5	2.036(2)	Co1-O1	2.0259(13)	Co1-O1W	2.082(2)	Co2-O3W	2.076(3)	Ni1-O2W	2.066(3)	Ni2-O4W	2.088(3)
Ni1-N2	2.044(2)	Co1-N9	2.2206(14)	Co1-O2W	2.100(3)	Co2-O4W	2.137(3)	Ni1-O1W	2.083(3)	Ni2-N4	2.110(4)
Ni1-O1	2.064(2)	Co1-N4	2.1041(15)	Co1-N2	2.146(3)	Co2-N13	2.143(3)	Ni1-N5	2.110(4)	Ni2-N8A	2.113(4)
Ni1-O2	2.080(2)			Co1-N9	2.160(3)	Co2-N8	2.149(3)	Ni1-N1A	2.117(4)	Ni2-O3W	2.115(4)
Ni1-N8	2.157(2)			Co1-N10	2.171(3)	Co2-N5	2.153(3)	Ni1-N8	2.146(4)	Ni2-N1	2.115(4)
Ni1-N1	2.164(2)			Co1-N1	2.186(3)	Co2 N16	2.159(3)	Ni1-N4A	2.148(4)	Ni2-N5A	2.128(4)
3b		**4a·**		**4c**		**5a**		**5b**		**5c**	
Bond	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**	**Bond**	**Length, A**
Co1-O1	2.064(3)	Ni1-N1	2.080(3)	Fe1-O1	2.115(2)	Ni1-N1	2.083(3)	Co1-O2	2.1123(12)	Fe1-O2	2.1204(14)
Co1-O2	2.105(3)	Ni1-N2	2.110(3)	Fe1-O8	2.121(2)	Ni1-O2	2.083(2)	Co1-O1	2.1245(13)	Fe1-O1	2.1534(15)
Co1-N11	2.139(4)	Ni1-N5	2.077(3)	Fe1-N2	2.157(3)	Ni1-O1	2.085(2)	Co1-N4	2.1309(15)	Fe1 N5	2.1736(17)
Co1-N14	2.156(4)	Ni1-N6	2.126(3)	Fe1-N6	2.163(3)	Ni1-N4	2.088(3)	Co1-N1	2.1380(15)	Fe1-N4	2.1737(17)
Co1-N27	2.178(4)	Ni1 O1	2.073(2)	Fe1-N5	2.201(3)	Ni1-N5	2.088(3)	Co1-N5	2.1399(15)	Fe1-N1	2.1764(17)
Co1-N18	2.182(4)	Ni1 O2	2.074(2)	Fe1-N1	2.215(3)	Ni1-N8	2.108(3)	Co1-N8	2.1418(15)	Fe1-N8	2.1772(18)

Refinement of crystal structures

Non-routine aspects of the structure refinement are as follows:

1a: positional disorder of the oxygen atoms over two positions of the nitrate anion (ratio of occupation factors 0.685: 0.315).

2b: positional disorder of the oxygen atoms over two positions of the nitrate anion (ratio of occupation factors 0.539: 0.461). The crystal structure contains heavily disordered nitrate anions and lattice water molecules, which were not possible to model reasonably and therefore the corresponding electron density was removed by SQUEEZE procedure in PLATON.

3a: positional disorder over two positions of two carbon atoms of the aliphatic chain of ligand (ratio of occupation factors 0.879: 0.121). Positional disorder over two positions of the oxygen atoms of the nitrate anion (ratio of occupation factors 0.543: 0.457). The crystal structure contains heavily disordered lattice water molecules, which was not possible to model reasonably and therefore corresponding electron density was removed by SQUEEZE procedure in PLATON.

4a and **4c**: the both crystal structures contain two lattice methanol molecules, which are disordered in a way that it was not possible to establish physically reasonable model, which would not lead to very short H···H contacts between the solvent and complex molecules. Therefore, we decided to remove corresponding electron density by SQUEEZE procedure in PLATON. Disorder of the oxygen atoms of perchlorate anion in **4a** was modelled (ration of occupation factors 0.624: 0.376) as positional disorder over two position, however, we believe that the nature of disorder is dynamic. This resulted in large displacement parameters and it was necessary to use constraints and restraints to build physically reasonable model. In **4c**, the fluorine atoms of the tetrafluoroborate anion also exhibit large displacement parameters but attempts to refine the structure involving positional disorder of these atoms did not bring any improvement in the resulting model, therefore we did not model the disorder.

5b and **5c**: positional disorder over two positions of the fluorine atoms of the tetrafluoroborate anion (ratio of occupation factors 0.957: 0.043 in **5b**, 0.947:0.053 in **5c**).

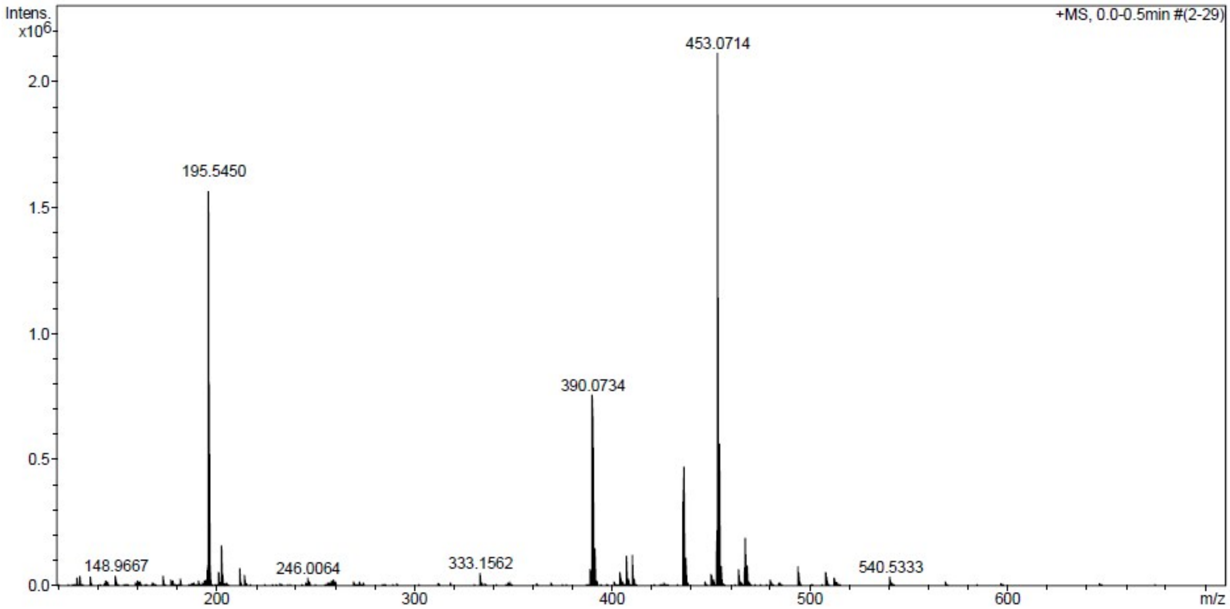

Fig. S1. ESI-MS spectra of 2b

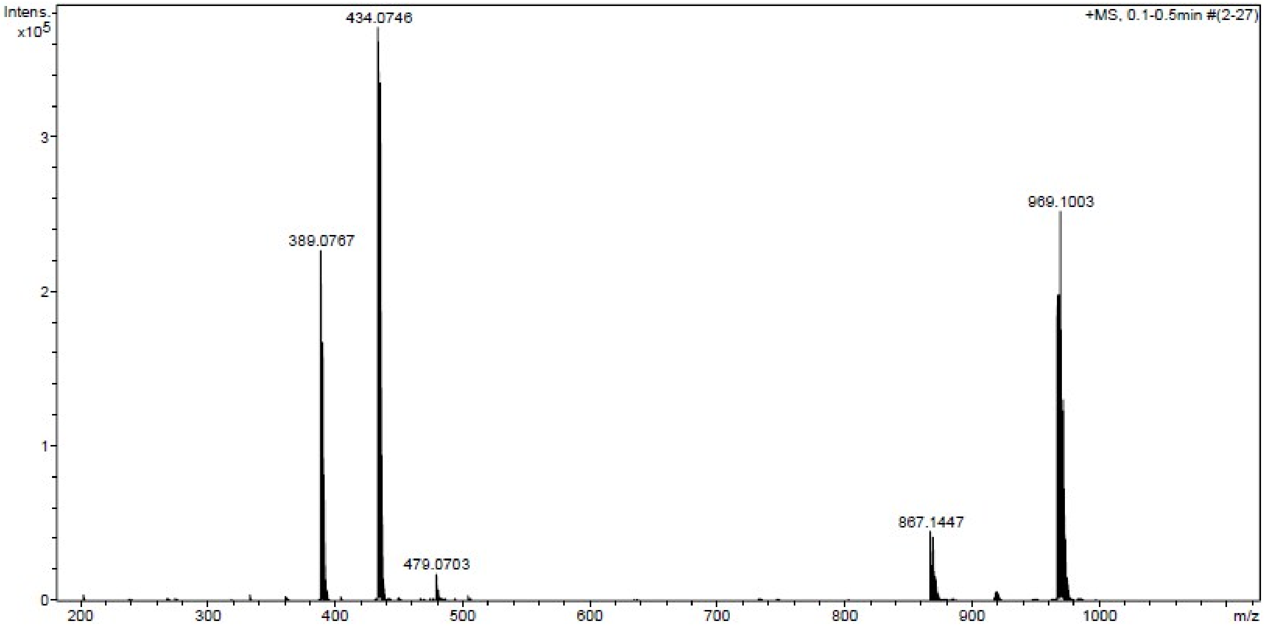

Fig. S2. ESI-MS spectra of 4a

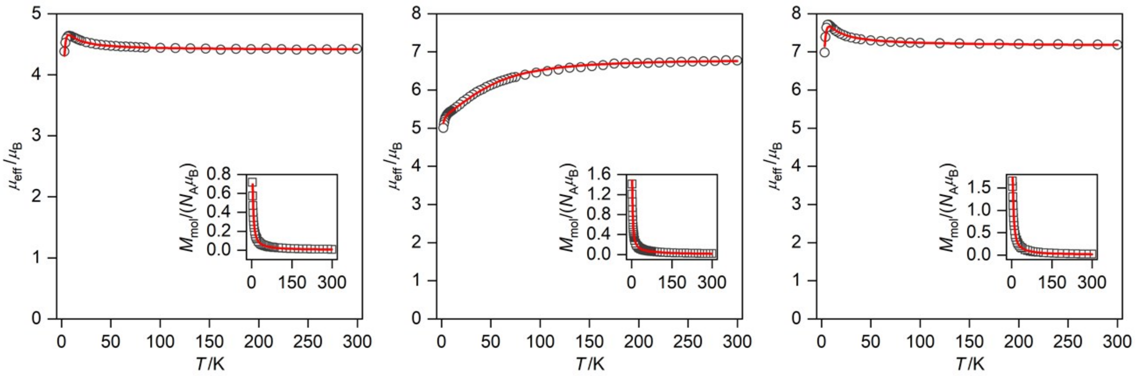

Fig.S3 Magnetic data for **3a** (*left*), **3b** (*middle*) and **3c** (*right*) depicted as temperature dependence of magnetic moment calculated from the molar magnetization measured at B = 0.5 T shown in the inset. Experimental data are shown as empty circles, fitted data are shown as red lines.

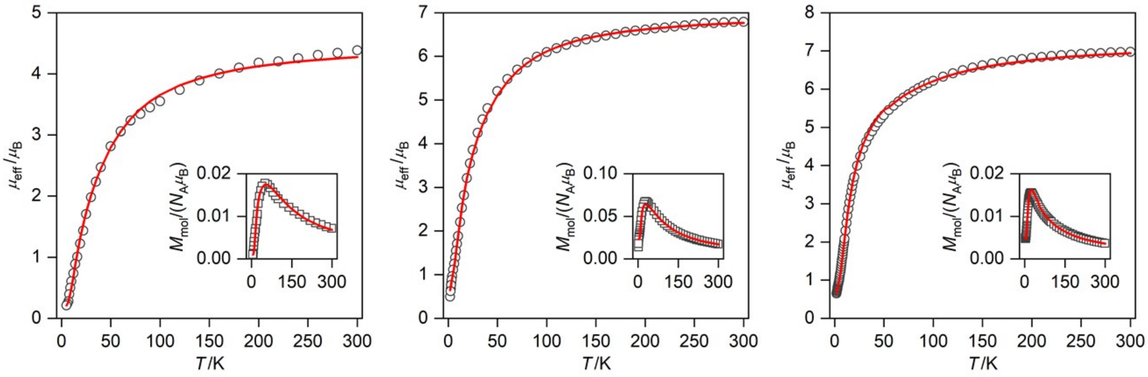

Fig.S4 Magnetic data for **5a** (*left*), **5b** (*middle*) and **5c** (*right*) depicted as temperature dependence of magnetic moment calculated from the molar magnetization measured at B = 0.5 T shown in the inset. Experimental data are shown as empty circles, fitted data are shown as red lines.

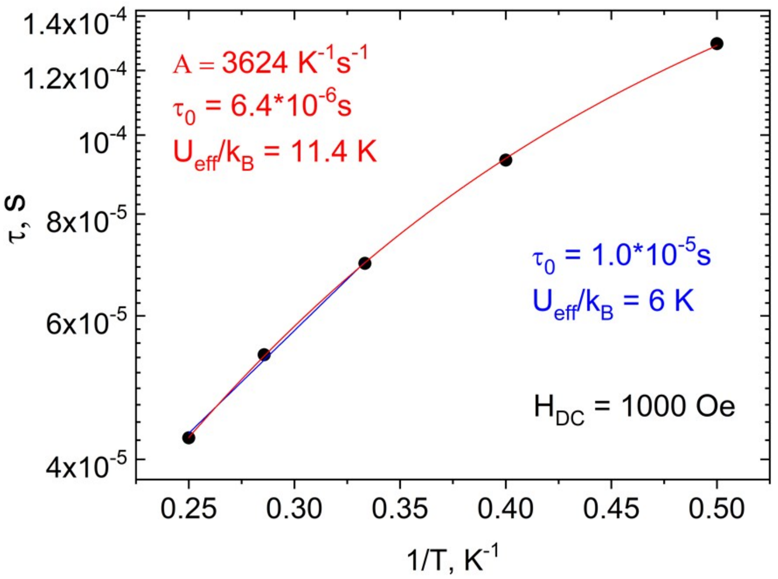

Fig. S5 The analysis of the relaxation timed derived from AC susceptibility data for **2b** with Arrhenius law (blue line) and with the combination of direct and Orbach processes (red line).

Discussion of the non-covalent interactions in the studied compounds.

Compounds **1a** and **1b**.

The both compounds **1a** and **1b** contain in the molecular structures of their complex molecules two aqua ligands in trans positions. In **1a**, one of the aqua ligands (O1) forms two bifurcated hydrogen bonds with the nitrate anions (symmetry related) with the following donor···acceptor distances (in Å): d(O1···O4S) = 2.689(6), d(O1···O5S) = 3.350(6); d(O1···O5S) = 3.005(5), d(O1···O6S) = 3.032(5). The second aqua ligand (O2) forms three hydrogen bonds with two lattice water molecules (O1W and O2W). In one of them, it acts as a hydrogen bonding acceptor (d(O1W···O2) = 2.902(3) Å), while in two other hydrogen bonds acts as a donor (in Å): d(O1W···O2) = 2.644(3), d(O2···O2W) = 2.705(3). The both triazolyl N-H groups (N3 and N7) form bifurcated N-H···O hydrogen bonds with the nitrate anions in a way that centrosymmetric dimers are formed (in Å): d(N3···O1S) = 2.853(3), d(N3···O1S) = 3.133(4); d(N7···O2S) = 2.860(4), d(N7···O3S) = 3.064(4), Besides the above mentioned hydrogen bonds, the lattice water molecules O1W and O2W form O-H···N (d(O1W···N6) = 2.807(3) Å) and bifurcated O-H···O hydrogen bonding (in Å, d(O2W···O6S) = 2.869(5), d(O2W···O6S) = 3.484(6); d(O2W···O1S) = 2.876(3), d(O2W···O6S) = 3.183(3)). All the hydrogen bonds are shown in Fig.S6.

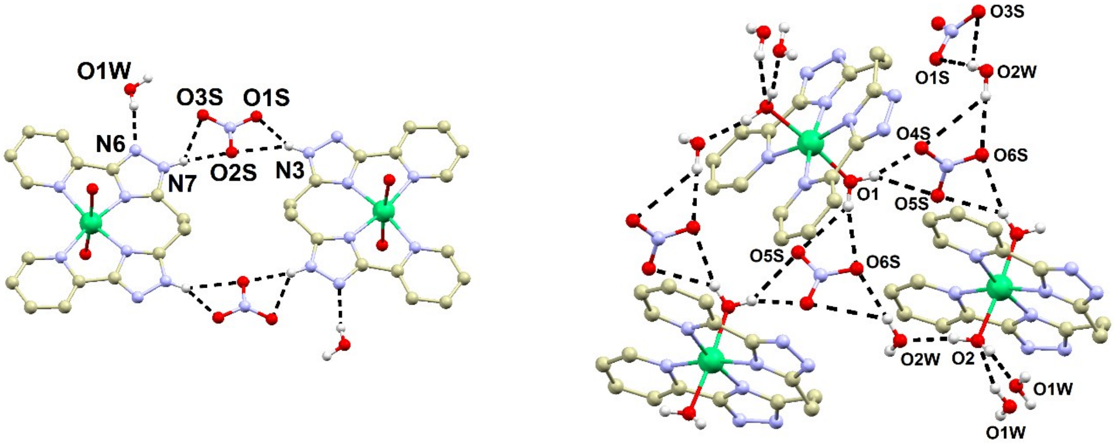

Fig. S6 Depiction of hydrogen bonding (black dashed lines) in **1a**: supramolecular dimer (*left*) and hydrogen bonding involving aqua ligands (*right*). Hydrogen atoms (except for those involved in hydrogen bonding) were omitted for clarity.

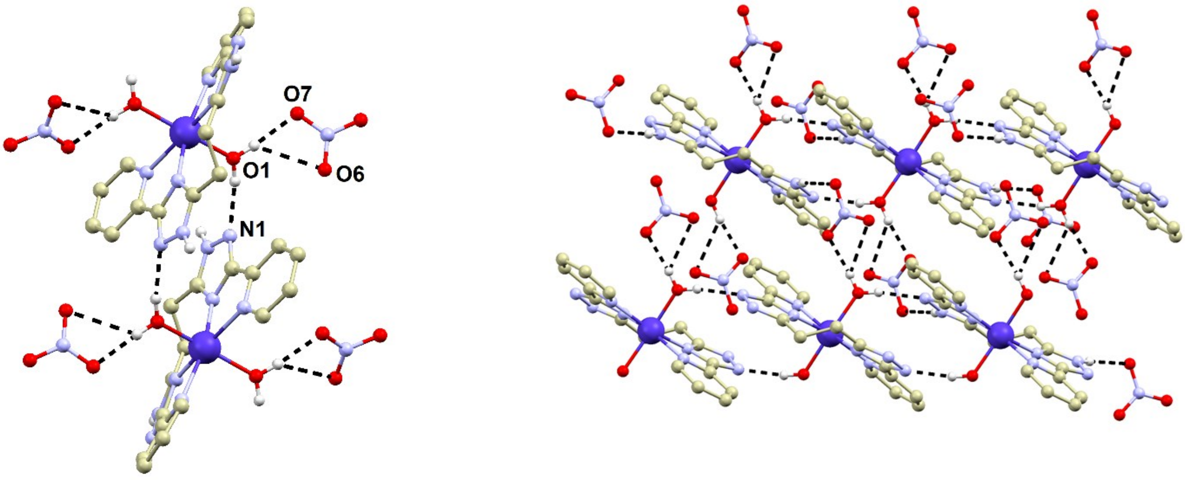

Fig. S7 Depiction of hydrogen bonding (black dashed lines) in **1b**: supramolecular dimer (*left*) and perspective view on fragment of the 2D supramolecular substructure (*right*). Hydrogen atoms (except for those involved in hydrogen bonding) were omitted for clarity.

In contrast to **1a**, the crystal structure of **1b** does not involve lattice aqua molecules and thus basic structural motif is different. Here, the centrosymmetric dimer is formed by O–H···N hydrogen bonding between the aqua ligand and triazolyl nitrogen atom of the adjacent complex molecule (*d*(O1···N1) = 2.758(2) Å). Since only the half of the complex molecule is symmetrically independent the dimers form chain supramolecular structure. The other hydrogen atom from the aqua ligand forms bifurcated O–H···O hydrogen bonding with nitrate anion (in Å, *d*(O1···O7) = 2.758(2) and *d*(O1···O6) = 3.129(2)). The N–H group from triazolyl ring forms N–H···O hydrogen bond with the third oxygen atom of the nitrate anion and thus extends the supramolecular structure to a layer. Hydrogen bonding in **1b** is shown in **Fig.S7**.

Compound **2b**.

Non-covalent contacts in **2b** cannot be described in full detail, because the crystal structure contains heavily disordered nitrate anions and lattice water molecules and the corresponding electron density was removed by SQUEEZE procedure in PLATON. However, it can be concluded that there is not a hydrogen bond interconnecting directly coordinating atoms, since the cis aqua ligands are involved in hydrogen bonding either with the lattice water molecules (O–H···O type, *d*(O···O) = 2.73 – 2.82 Å) or triazolyl nitrogen atoms (O–H···N type, *d*(O···N) = 2.84 - 2.90 Å). The neighboring complex molecules interacts via offset and twisted π-π stacking of the pyridyl rings (the shortest C···C distance of 3.27 Å) or whole pyridyl-triazolyl moieties (the shortest C···C distance of 3.30 Å, the shortest C···N distance of 3.22 Å). Hydrogen bonding in **2b** is shown in **Fig.S8**.

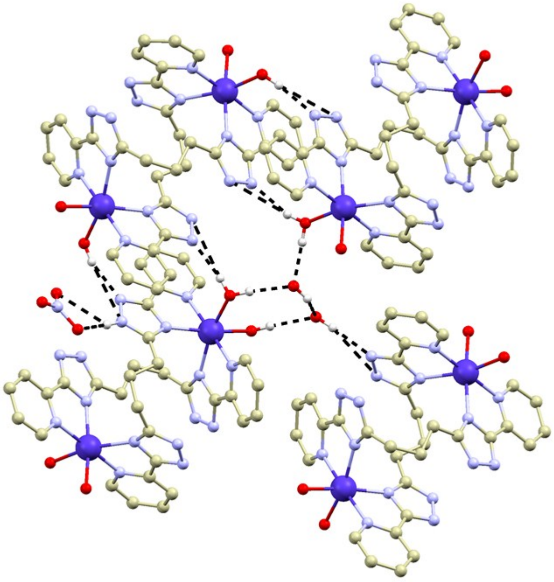

Fig. S8 Depiction of hydrogen bonding (black dashed lines) in **2b**. Hydrogen atoms (except for those involved in hydrogen bonding) were omitted for clarity.

Compounds **3a** and **3b**.

The crystals of **3a** suffered from partial lattice solvent loss and therefore, electron density of some solvent molecules had to be removed by SQUEEZE procedure in PLATON. The N–H···O hydrogen bonding in **3a** is formed between three N–H groups of triazolyl rings and three nitrate anions (in Å, *d*(N···O) = 2.885(5); bifurcated: 2.791(5) and 3.402(6); bifurcated: 2.997(7) and 3.008(7), **Fig.S9** left). The fourth N–H group forms N–H···O hydrogen bond with the lattice water molecule (*d*(N···O) = 2.747(5) Å), which creates two other O–H···O hydrogen bonds with two different nitrate anions (in Å, *d*(O···O) = 2.904(5) Å; bifurcated: 2.797(5) and 3.372(6), **Fig.S9** left). The cis aqua ligands form O–H···O hydrogen bonds (single or bifurcated, **Fig.S9** right) with O···O distances ranging between 2.68 and 2.97 Å. In the case of bifurcated hydrogen bonds, the O···O distances of the second formed contact are significantly longer (3.09 - 3.28 Å). One of the aqua ligands forms O–H···O hydrogen bond with the lattice water molecule (2.763(8) Å), which further forms O–H···N contact with nitrogen atom from the triazolyl ring (2.997(9) Å, **Fig.S9** right). The complex molecules in **3a** do not form significant ring-ring stacking interactions.

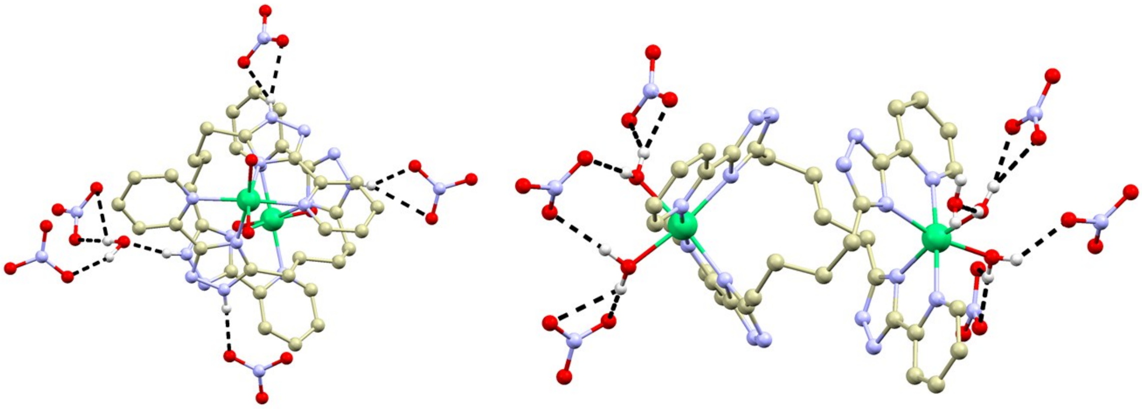

Fig. S9 Depiction of hydrogen bonding (black dashed lines) in **3a**: hydrogen bonding formed by N–H triazolyl groups (*left*), O–H···O hydrogen bonding formed by the aqua ligands. Hydrogen atoms (except for those involved in hydrogen bonding) were omitted for clarity.

The non-covalent contacts in **3b** are in general very similar to those in **3a**, but with the difference that crystals of **3b** did not suffer by the solvent loss and therefore the crystal structure contains more lattice water molecules. Furthermore, the asymmetric unit contains two halves of the complex molecules (Co1 and Co2), each containing two cis aqua ligands and one triazolyl-pyridyl ligand, which are rich donors and acceptors of hydrogen bonding. Thus, the resulting crystal structure is complicated 3D supramolecular framework. For the purposes of this article, we will keep focused just on main features, which could influence magnetic behavior. The both complex molecules in asymmetric unit form supramolecular dimers supported by the ring-ring stacking interactions of the pyridyl-triazolyl moieties. Interestingly, both supramolecular dimers differ structurally. Dimers involving Co1 complex molecules are formed by hydrogen bonding in which the lattice water molecules act as linkers between the cis aqua ligands and nitrogen atoms of two triazolyl rings (**Fig. S10** left). The O–H···O hydrogen bonds are rather short with *d*(O–H···O) = 2.762(5) and 2.796(6) Å. The O–H···N hydrogen bonds are a bit longer: *d*(O–H···N) = 2.871(6) and 3.045(6) Å. The π-π interactions of the pyridyl-triazolyl moieties have the shortest C···C distance of 3.357(7) Å.

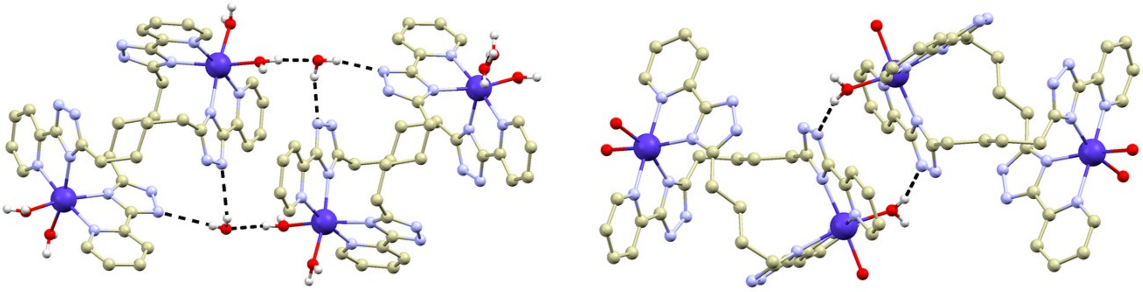

Fig. S10 Depiction of hydrogen bonding (black dashed lines) in **3b**: supramolecular dimer involving Co1 molecules (*left*) and Co molecules (*right*). Hydrogen atoms (except for those involved in hydrogen bonding) were omitted for clarity.

Dimers involving Co2 complex molecules are formed by N–H···O hydrogen bonding between one of the aqua ligands and triazolyl nitrogen atoms (**Fig. S10** right) with *d*(N···O) distance of 2.813(4) Å. Again, the offset π-π stacking interactions between the adjacent pyridyl-triazolyl moieties are present within a dimer with the shortest C···C distance of 3.478(6) Å.

Other non-covalent interactions presented in the crystal structure of **3b** are very similar to those observed for previously discussed compounds and mainly hydrogen bonding between lattice water molecules, aqua ligands and water molecules, water molecules and nitrate anions or triazolyl N–H groups and nitrate anions are observed.

Compounds **4a** and **4c**.

The methanol molecules in the crystal structures of **4a** and **4c** (complexes are isostructural) were heavily disordered. It was possible to (partially satisfactorily) model this issue by using constraints and restraints but resulting solution did not provide physically reasonable model without very short H···H contacts (classified as A-alerts in checkcif) originated in hydrogen atoms of the solvent molecules. Therefore, we decided to remove electronic density of the methanol molecules by SQUEEZE procedure in PLATON. Non-covalent contacts not involving lattice solvent molecules are weak including mainly C–H···O and C–H···π interactions. Remarkably, the interactions between the neighboring complex molecules are provided by short N···N contacts (**Fig. S11**) between the triazolyl nitrogen atoms. These rather short interactions (in Å, *d*(N···N) = 2.867(5) in **4a**, 2.903(5) in **4c**) are most probably hydrogen bonding with disordered hydrogen atoms between positions 1 and 2 in triazolyl rings.

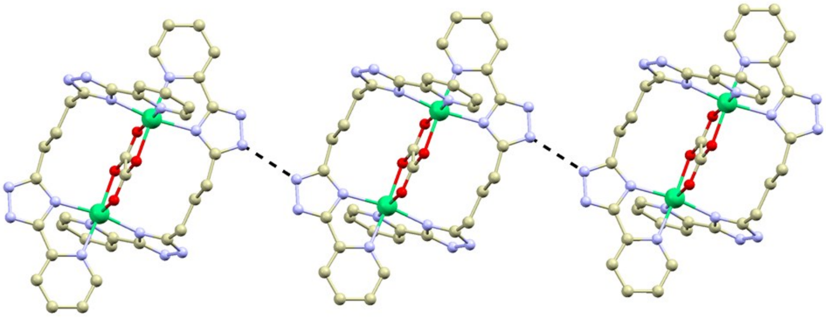

Fig. S11 Depiction of N···N interactions (black dashed lines) in **4a**. Hydrogen atoms (except for those involved in hydrogen bonding) were omitted for clarity.

Compounds **5a**-**c**.

In the crystal structures of **5a-c** (complexes are isostructural) the most important non-covalent contacts are provided by hydrogen bonding involving complex molecules, anions (ClO_4^- in **5a**, BF_4^- in **5b** and **5c**) and lattice solvent molecules (acetone and water). Connection between neighboring complex molecules in crystal structures of **5a-c** is provided by two lattice water molecules, when one of them form N–H···O hydrogen bonding (as hydrogen bonding acceptor) with triazolyl N–H group (in Å, *d*(N···O) = 2.681(6) in **5a**, 2.681(3) in **5b**, 2.677(3) in **5c**). This water molecule further forms two O–H···O hydrogen bonds, one with the acetone molecule (in Å, *d*(O···O) = 2.854(4) in **5a**, 2.834(3) in **5b**, 2.820(2) in **5c**) and the second with another lattice water molecule (in Å, *d*(O···O) = 2.695(6) in **5a**, 2.713(3) in **5b**, 2.720(4) in **5c**). This also forms two O–H···O/F hydrogen bonds, one with the oxalate ligand (in Å, *d*(O···O) = 2.853(4) in **5a**, 2.888(2) in **5b**, 2.887(2) in **5c**) and the second with the anion (in Å, *d*(O···O) = 2.827(7) in **5a**, *d*(O···F) = 2.779(3) in **5b**, 2.752(4) in **5c**). The anion is further stabilized by hydrogen bonding between N–H group of triazolyl groups and oxygen/fluorine atom of the anion (*d*(N···O) = 2.872(6) in **5a**, *d*(N···F) = 2.818(3) in **5b**, 2.819(4) in **5c**).

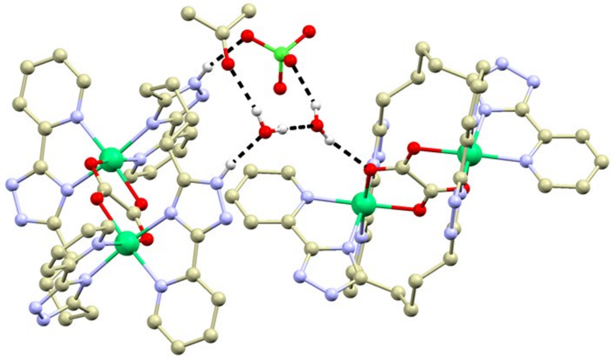

Fig. S12 Depiction of hydrogen bonding (black dashed lines) in **5a**. Hydrogen atoms (except for those involved in hydrogen bonding) were omitted for clarity.