Supplementary Information (SI) for CrystEngComm.

Electronic supplementary information

for

The role of alkali metal cations in construction of heterometallic Ni^{II} polymeric cyclopropane-1,1-dicarboxylates

Ekaterina N. Zorina-Tikhonova,[*a,b] *Anna K. Matiukhina,*[a] *Alexander A. Korlyukov,*[c] *Alexander S. Goloveshkin,*[c] *Konstantin A. Babeshkin,*[a] *Nikolay N. Efimov,*[a,b] *Eugeny V. Alexandrov,*[d] *Mikhail A. Kiskin*[a] *and Igor L. Eremenko*[a,c]

[a]N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Leninsky Prosp. 31, Moscow 119991, Russian Federation. ezorinatikhonova@igic.ras.ru

[b]HSE University, Myasnitskaya 20, Moscow 101000, Russian Federation

[c]A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilov St. 28, Moscow 119334, Russian Federation

[d]Center NTI "Digital Materials Science: New Materials and Substances", Bauman Moscow State Technical University, 2nd Baumanskaya st. 5/1, Moscow 105005, Russian Federation

Crystallographic Data Collection and Structure Refinement

X-ray diffraction analysis was carried out on a Bruker Apex-II CCD diffractometer (graphite monochromator, MoKα radiation, $\lambda = 0.71073$ Å). An absorption correction was applied empirically using the SADABS program [1] and all structures were solved using the SHELXT program [2]. All nonhydrogen atoms were localized from the difference Fourier maps and refined by F^2_{hkl}, using OLEX^2 1.5 and SHELXL programs [3-4]. All nonhydrogen atoms were refined in anisotropic approximation. Hydrogen atoms of methyl and water fragments were calculated according to the idealized geometry and refined with constraints applied to C–H and O–H bond lengths and equivalent displacement parameters ($U_{iso}(H) = 1.2U_{eq}(C)$; $U_{iso}(H) = 1.5U_{eq}(O)$). In complexes **3** the difference map also shows the presence of severely disordered solvent molecules. In the unit cell the volume is 93.9 Å^3 for an electron count of 35.1 which corresponds to 3.5 water molecules. This was removed by using SQUEEZE option in PLATON [5]. For complex **4**, extinction was additionally taken into account, the coefficient is 0.0559(18).

CCDC numbers 2161741 (**1**), 2161742 (**2**), 2161732 (**3**), 2161733 (**4**) contain the supplementary crystallographic data for the compounds reported. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Crystallography parameters and refinement details are given in Table S1.

Table S1. Crystallography parameters and refinement details.

parameters	**1**	**2**	**3**	**4**
formula	$\{[Na_2Ni(cpdc)_2(H_2O)_6]{\cdot}4H_2O\}_n$	$\{[K_6Ni_3(cpdc)_6(H_2O)_{10}]{\cdot}8H_2O\}_n$	$[Rb_6Ni_3(cpdc)_6(H_2O)_{12}]{\cdot}5.5H_2O\}_n$	$[Cs_2Ni(cpdc)_2(H_2O)_8]_n$
brutto formula	$C_{10}H_{28}Na_2NiO_{18}$	$C_{30}H_{60}K_6Ni_3O_{42}$	$C_{30}H_{59}Ni_3O_{41.5}Rb_6$	$C_{10}H_{24}Cs_2NiO_{16}$
M, g/mol	541.01	1503.51	1772.72	724.82
temperature, K	120	184.15	120	296.15
crystal system	triclinic, $P\bar{1}$			
space group				
unit cell parameters	a = 5.5034(7) Å	a = 10.2896(18) Å	a = 10.5074(11) Å	a = 5.2628(2) Å
	b = 8.4085(11) Å	b = 12.302(2) Å	b = 12.4178(13) Å	b = 10.5543(4) Å
	c = 11.8303(15) Å	c = 12.719(2) Å	c = 12.4907(13) Å	c = 10.7212(4) Å
	α = 81.350(2)°	α = 75.425(3)°	α = 78.142(2)°	α = 114.6160(10)°
	β = 87.308(2)°	β = 66.665(2)°	β = 66.982(2)°	β = 92.6790(10)°
	γ = 83.679(2)°	γ = 78.791(3)°	γ = 78.702(2)°	γ = 101.051(2)°
volume, Å^3	537.68(12)	1422.5(4)	1455.9(3)	525.98(3)
D, g/cm^3	1.671	1.755	2.022	2.288
μ (mm^{-1})	1.027	1.529	6.047	4.407

T_{min}/T_{max}	0.4876/0.7461	0.5506/0.7461	0.5108/0.7465	0.4821/0.7471
F(000)	282	774	877	350
θ range,°	1.742-30.624	1.720-28.282	1.690-30.647	2.182-35.915
reflection collected/unique/[$I>2\sigma(I)$]	7283/3254/3109	14737/7002/5520	26265/8965/7751	7897/4207/3636
R_{int}	0.0260	0.0309	0.0254	0.0293
goodness-of-fit	1.168	1.043	1.038	1.038
R [$I > 2\sigma(I)$]	$R_1 = 0.0393$ $wR_2 = 0.1086$	$R_1 = 0.0423$ $wR_2 = 0.0948$	$R_1 = 0.0210$ $wR_2 = 0.0496$	$R_1 = 0.0318$ $wR_2 = 0.0639$
R [all data]	$R_1 = 0.0406$ $wR_2 = 0.1092$	$R_1 = 0.0568$ $wR_2 = 0.1012$	$R_1 = 0.0280$ $wR_2 = 0.0517$	$R_1 = 0.0400$ $wR_2 = 0.0673$

Powder X-ray diffraction

The powder patterns (Fig. S1, S2) were collected on a Bruker D8 Advance diffractometer equipped with variable slits, Ni filter (CuKα radiation) and 1D LynxEye detector. The patterns were obtained in the reflection mode (Bragg-Brentano geometry) with the sample rotation, step size 0.02° 2θ. The patterns were refined using the Rietveld approach in TOPAS 5 software.

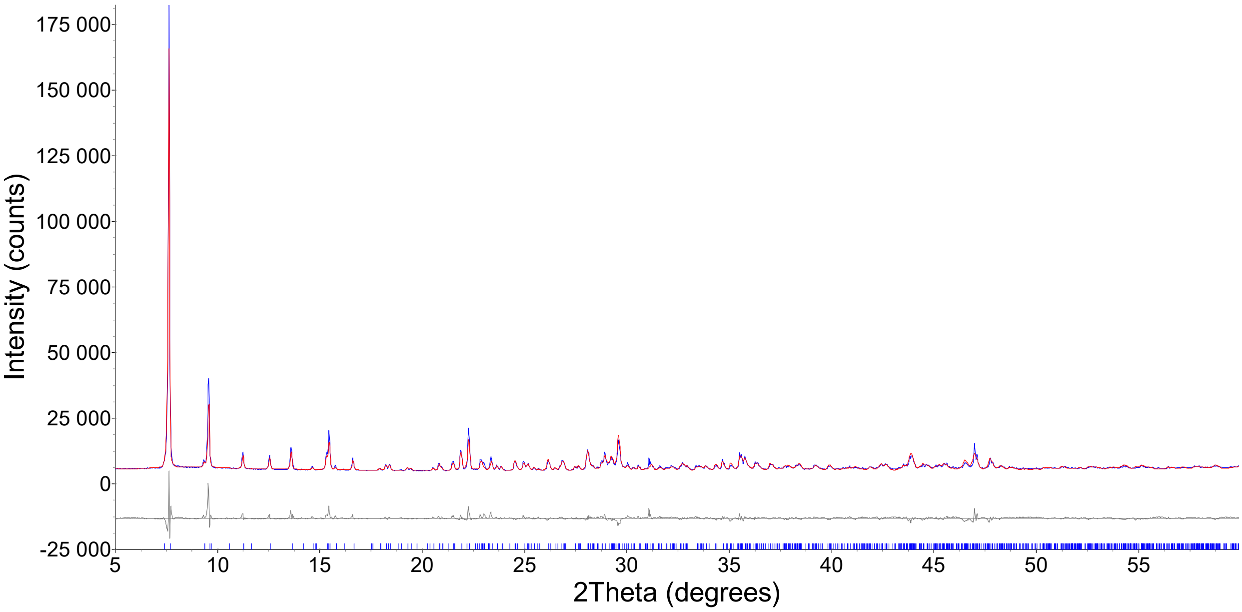


Figure S1. Rietveld fit (red line) of powder pattern of **2** (blue line) and their difference (grey line).

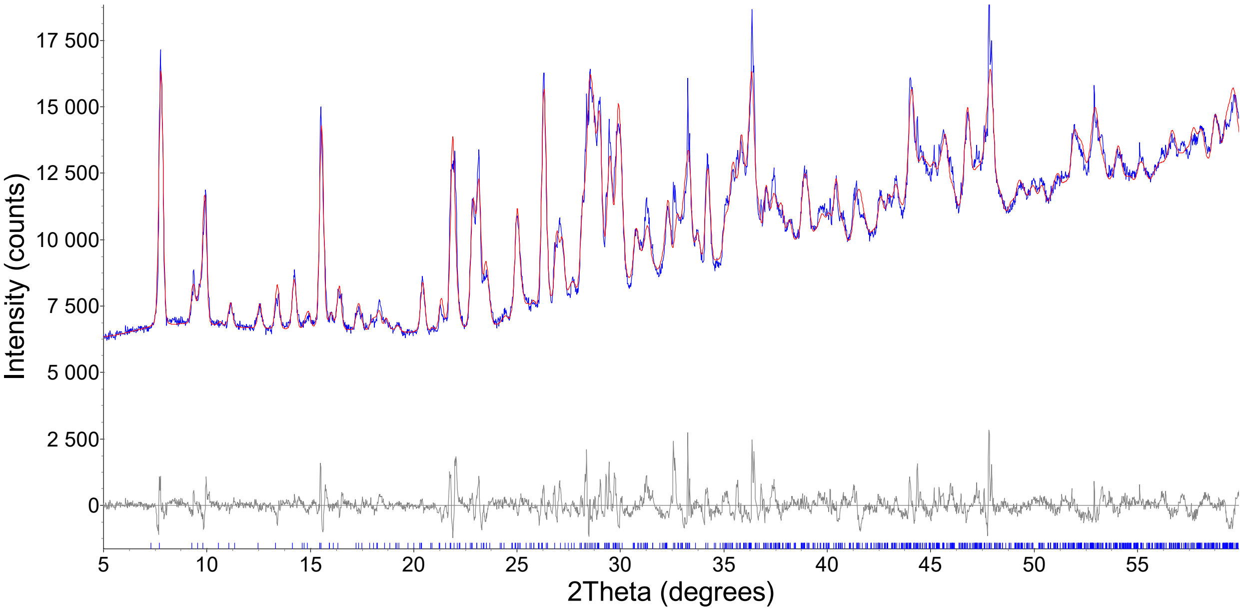


Figure S2. Rietveld fit (red line) of powder pattern of **3** (blue line) and their difference (grey line).

The geometry of the coordination environment of metal atoms was calculated using the SHAPE program [6], based on the analysis of X-ray diffraction experimental data.

Table S2. Atom polyhedral of Ni^{II} and alkali metals and their deviations from ideal geometry (CShM).

	1	**2**	**3**	**4**
Ni1	OC-6 [0.114]	OC-6 [0.016]	OC-6 [0.021]	OC-6 [0.110]
Ni2		OC-6 [0.128]	OC-6 [0.126]	
$M^{I}1$	OC-6 [2.543]	TPR-6 [3.373]	COC-7 [3.427]	JSPC-10 [7.559]
$M^{I}2$		CTPR-7 [3.599]	BTPR-8 [2.855]	
$M^{I}3$		TBPY-5 [11.826]	COC-7 [8.736]	

OC-6 – octahedron; PPY-6 – pentagonal pyramid; TPR-6 – trigonal prism; COC-7 – capped octahedron; BTPR-8 biaugmented trigonal prism; JSPC-10 – sphenocorona

Table S3. Symmetry group distortion for polyhedra for complexes **2-3**.

	2		**3**	
	Ni1	Ni2	Ni1	Ni2
O_h	0.0160	0.0846	0.0177	0.0818
D_{4h}	0.0088	0.0818	0.0070	0.0749
D_{2h}	0.0089	0.0812	**0.0050**	0.0753
D_{2d}	0.0088	0.0860	0.0085	**0.0655**
C_{4v}	**0.0073**	0.0776	0.0085	0.0823
C_{2v}	0.0096	**0.0721**	0.0055	0.0696

Methods of Underlying Topology Analysis

Topological characteristics of coordination compounds are important in designing new networks and searching for 'structure-properties' correlations [7-10]. This approach has been used to design magnetic coordination compounds [11]. The main computational tools for topological analysis have been implemented in program package ToposPro [12]. Underlying topology of a crystal structure can be described by simple connected periodic graph which nodes represent bodycenters of building units (coordination centers, ligands, complex groups, counterions, clathrate molecules), and edges represent interactions between them (covalent, H-bonding, halogen bonds, columbic, magnetic, etc.). Such a graph is called an underlying net, and the choice of building units and interactions between them determines the topological representation of the structure [13-16].

A net of coordination bonds and ionic interactions ensures the connectivity of metal coordination centers, ligands and counterions: each component is represented by a node of simplified net, and a pairwise bond or the interactions between them are represented by an edge of simplified net. In the net of ionic interactions, the complex ion and counterion are represented as nodes and the pairwise interactions between them are represented as edges. In the net of ionic interactions and H-bonds, additional edges are related to H-bonds and additional nodes are related to H-bonded clathrate molecules and molecular ions. The net of magnetic interactions considers only paramagnetic centers as nodes. An edge is established between two paramagnetic centers if solid angle value of Voronoi face is larger than 1.5%. Voronoi polyhedra in this case are constructed only for paramagnetic centers both as central atoms and atoms of the environment, while all other atoms are ignored for this construction. Therefore, the net of magnetic interactions represents the topology of pairwise interactions for the nearest paramagnetic centers in crystal space.

The analysis of structural correlations becomes more efficient with involving all known structures of the type under consideration. The best source of crystal structure data for coordination compounds is Cambridge Structural Database (CSD) [17-18]. Automatic analysis of numerous crystal structures from CSD (release of November 2022) with ToposPro shows the variety of their topologies.

Magnetic Susceptibility Measurements

The magnetic susceptibility measurements of complexes **2** and **3** were investigated on a Quantum Design PPMS-9 magnetometer. For the temperature range was 2-300 K in constant external magnetic field 5000 Oe. All studies of magnetic behavior were carried out on polycrystalline milled samples sealed in plastic bags and frozen in mineral oil to prevent crystallite orientation under the influence of a magnetic field. The paramagnetic component of the magnetic susceptibility (χ) was determined taking into account both the diamagnetic contribution of the sample itself, estimated from the Pascal constant, and the diamagnetic contributions of the mineral oil and the holder.

Quantum chemical calculations

Ab initio (post Hartree-Fock) calculations of ZFS parameters and g-tensor were performed based on state-averaged complete-active-space self-consistent-field (SA-CASSCF) wave function, [19] complements by N-electron valence second-order perturbation theory (NEVPT2) [20], using the ORCA program package (version 5.0.1) [21]. The calculations were performed with the geometry of the experimentally determined X-ray structures. The active space of the CASSCF calculations was composed of eight electrons in five d-orbitals of Ni^{2+} ions ($S = 1$): CAS(8,5). The state-averaged approach was used, in which all 10 triplets and 15 singlets states were averaged with equal weights. The polarized triple-ʒ-quality basis set def2-TZVP was used for all atoms [22]. An auxiliary def2/JK Coulomb fitting basis set was used in the calculation [23]. ZFS parameter, based on dominant spin-orbit coupling contributions from excited states, was calculated using quasi-degenerate perturbation theory (QDPT) [24], in which an approximation to the Breit-Pauli form of the spin-orbit coupling operator (SOMF) [25] and an effective Hamiltonian approach are examined [26]. The splitting of the d-orbitals was analysed within the *ab initio* ligand field theory (AILFT) [27-28]. Five separated d-orbitals are described as linear combinations of the d-orbitals. Splitting is presented based on the largest coefficients for each orbital.

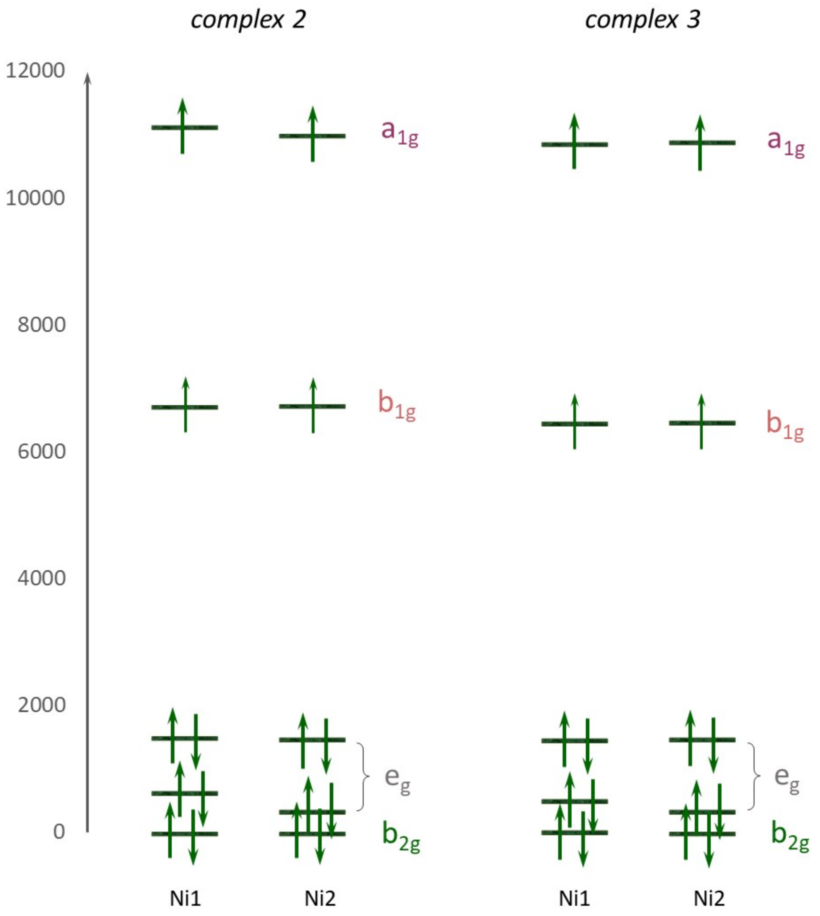
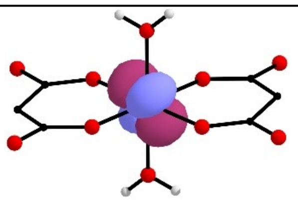
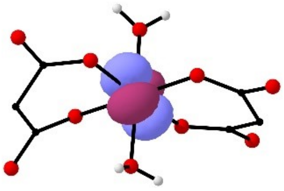
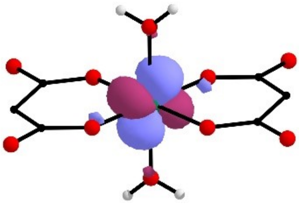
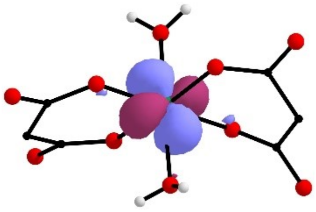
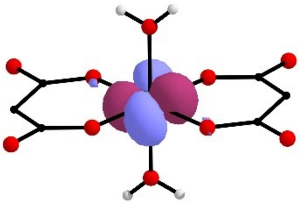
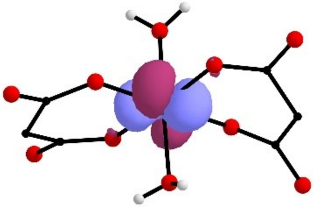
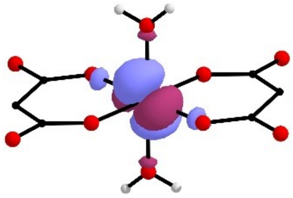
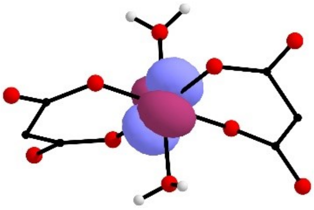
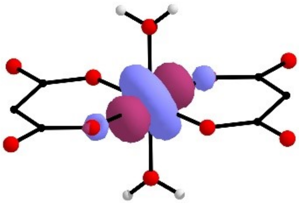
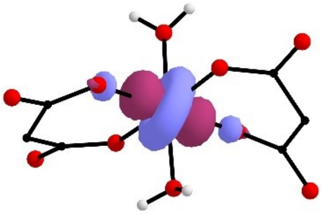
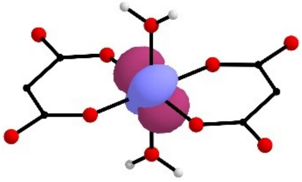
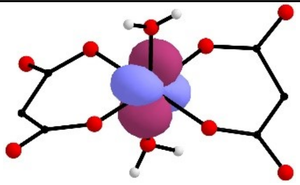
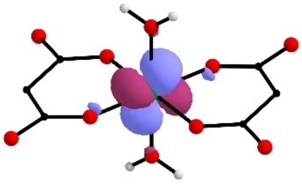
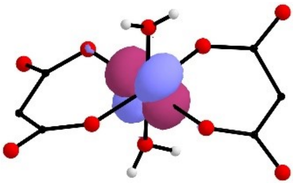
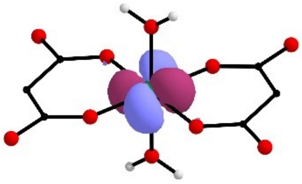
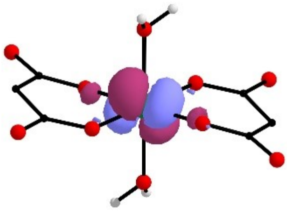
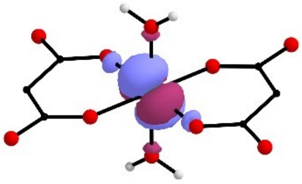
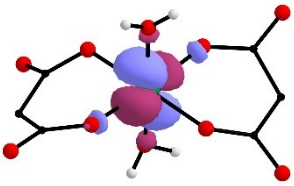
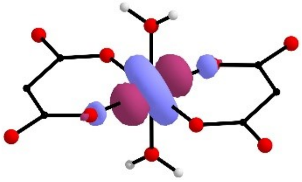
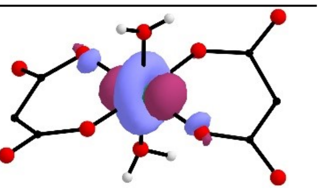


Figure S3. Orbital energies computed for the ground state of **2** and **3**, using CASSCF/NEVPT2. The arrangement of the orbitals corresponds to the largest contribution.

Table S4. CASSCF/NEVPT2 calculated relative energy (cm^{-1}) and type of 3d-orbitals for each Ni^{2+} ion in complexes **2-3**.

		Complex 2			
Ni1			Ni2		
0	*dxy*		0	*dxy*	
599.6	*dyz*		349.0	*dyz*	

1497.7	*dxz*		1465.0	*dxz*	
6751.5	dx^2-y^2		6787.1	dx^2-y^2	
11186.3	dz^2		11025.9	dz^2	
Complex 3					
Ni1			Ni2		
0	*dxy*		0	*dxy*	
500.9	*dyz*		330.4	*dyz*	
1468.9	*dxz*		1479.8	*dxz*	
6492.6	dx^2-y^2		6506.6	dx^2-y^2	

10942.0	dz^2		10917.1	dz^2	

References

1. G. M. Sheldrick, *SADABS. Madison (WI, USA): Bruker AXS Inc.*
2. G. M. Sheldrick, *Acta Crystallogr. A* 2015, **71**(1), 3. Doi: 10.1107/S2053273314026370
3. G. M. Sheldrick, *Acta Crystallogr. C* 2015, **71**(1), 3. Doi: 10.1107/S2053229614024218
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339. Doi: 10.1107/S0021889808042726
5. A. L. Spek, *Acta Crystallogr. C* 2015, **71**, 9. Doi: 10.1107/S2053229614024929
6. M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, *Universitat de Barcelona: Barcelona, Spain* 2013.
7. N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.* 2005, **38**(3), 176. Doi: 10.1021/ar020022l
8. M. O'Keeffe and O. M. Yaghi, *Chem. Rev.* 2012, **112**(2), 675. Doi: 10.1021/cr200205j
9. E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio, *CrystEngComm,* 2011, **13**, 3947–3958. Doi: 10.1039/c0ce00636j
10. A. P. Shevchenko, E. V. Alexandrov, A. A. Golov, O. A. Blatova, A. S. Duyunova and V. A. Blatov, *Chem. Commun.* 2020, **56**, 9616. Doi: 10.1039/d0cc04004e
11. J.-P. Zhao, S.-D. Han, X. Jiang, J. Xu, Z. Chang and X.-H. Bu, *Chem. Commun.* 2015, **51**, 4627. Doi: 10.1039/c4cc09547b
12. V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.* 2014, **14**(7), 3576. Doi: 10.1021/cg500498k
13. M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.* 2008, **41**(12), 1782. Doi: 10.1021/ar800124u
14. E. V. Alexandrov, A. P. Shevchenko, N. A. Nekrasova and V. A. Blatov, *Russ. Chem. Rev.* 2022, **91**(4), RCR5032. Doi: 10.1070/rcr5032
15. A. P. Shevchenko, A. A. Shabalin, I. Yu. Karpukhin and V. A. Blatov, *Sci. Technol. Adv. Mater.* 2022, **2**(1), 250. Doi: 10.1080/27660400.2022.2088041
16. E. V. Alexandrov, A. P. Shevchenko and V. A. Blatov, *Cryst. Growth Des.* 2019, **19**(5), 2604. Doi: 10.1021/acs.cgd.8b01721

17. P. Z. Moghadam, A. Li, X.-W. Liu, R. Bueno-Perez, S.-D. Wang, S. B. Wiggin, P. A. Wood and D. Fairen-Jimenez, *Chem. Sci.* 2020, **11**, 8373–8387. Doi: 10.1039/d0sc01297a

18. M. A. Agafonov, E. V. Alexandrov, N. A. Artyukhova, G. E. Bekmukhamedov, V. A. Blatov, V. V. Butova, Y. M. Gayfulin, A. A. Garibyan, Z. N. Gafurov, Yu. G. Gorbunova, L. G. Gordeeva, M. S. Gruzdev, A. N. Gusev, G. L. Denisov, D. N. Dybtsev, Yu. Yu. Enakieva, A. A. Kagilev, A. O. Kantyukov, M. A. Kiskin, K. A. Kovalenko, A. M. Kolker, D. I. Kolokolov, Y. M. Litvinova, A. A. Lysova, N. V. Maksimchuk, Y. V. Mironov, Yu. V. Nelyubina, V. V. Novikov, V. I. Ovcharenko, A. V. Piskunov, D. M. Polyukhov, V. A. Polyakov, V. G. Ponomareva, A. S. Poryvaev, G. V. Romanenko, A. V. Soldatov, M. V. Solovyeva, A. G. Stepanov, I. V. Terekhova, O. Yu. Trofimova, V. P. Fedin, M. V. Fedin, O. A. Kholdeeva, A. Yu. Tsivadze, U. V. Chervonova, A. I. Cherevko, V. F. Shul′gin, E. S. Shutova and D. G. Yakhvarov, *J. Struct. Chem.* 2022, **63**, 671. Doi: 10.1134/s0022476622050018

19. P.-Å. Malmqvist and B. O. Roos, *Chem. Phys. Lett.* 1989, **155**(2), 189. Doi: 10.1016/0009-2614(89)85347-3

20. C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger and T. J.-P. Malrieu, *J. Chem. Phys.* 2001, **114**(23), 10252. Doi: 10.1063/1.1361246

21. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 2012, **2**(1), 73. Doi: 10.1002/wcms.81

22. A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.* 1994, **100**(8), 5829. Doi: 10.1063/1.467146

23. F. Neese, *J. Comput. Chem.* 2003, **24**(14), 1740. Doi: 10.1002/jcc.10318

24. D. Ganyushin and Neese, *J. Chem. Phys.* 2006, **125**(2), 024103. Doi: 10.1063/1.2213976

25. F. Neese, *J. Chem. Phys.* 2005, **122**(3), 034107. Doi: 10.1063/1.1829047

26. R. Maurice, R. Bastardis, C. de Graaf, N. Suaud, T. Mallah and N. Guihéry, *J. Chem. Theory Comput.* 2009, **5**(11), 2977. Doi: 10.1021/ct900326e

27. D. M. P. Mingos, P. Day and J. P. Dahl, *Springer, Berlin/Heidelberg, Germany,* 2012. Doi: 10.1007/978-3-642-27378-0

28. S. K. Singh, J. Eng, M. Atanasov and F. Neese, *Coord. Chem. Rev.* 2017, **344**, 2. Doi: 10.1016/j.ccr.2017.03.018