Supporting materials

Iron molybdenum nitrilotriacetate and iminodiacetate – spectroscopy, structural characterization and CO_2 adsorption

Si-Yuan Wang,[a] Xin Dong, [a] Jun-Fei Chen,[b] Zhao-Hui Zhou[a,]*

a. State Key Laboratory for Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China
b. State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Ningxia, 750021, China

Figure and Table Options

MoO_4 and Fe-ida mononuclear units as connected nodes in $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *a* axis. Color codes: teal for MoO_4 units 4-connected nodes, yellow for Feida mononuclear units 5-connected nodes.

Figure S18. Schematic description of the equivalent topology framework with a 4,5-connected dinodalnbo-x-d/I m -3 m->I -4 2 m topological motif considering the MoO_4 and Feida mononuclear units as connected nodes in $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *b* axis. Color codes: teal for MoO_4 units 4-connected nodes, yellow for Fe-ida mononuclear units 5-connected nodes.

Figure S19. Schematic description of the equivalent topology framework with a 4,5-connected dinodalnbo-x-d/I m -3 m->I -4 2 m topological motif considering the MoO_4 and Feida mononuclear units as connected nodes in $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *c* axis. Color codes: teal for MoO_4 units 4-connected nodes, yellow for Fe-ida mononuclear units 5-connected nodes.

Table S1. Crystallographic data and structural refinements for complexes $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot16H_2O$ (**1**), $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**), $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot16H_2O$ (**3**) and $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot16H_2O$ (**4**).

Table S2. Selected bond distances (Å) and angles (°) within the water layers in $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot16H_2O$ (**1**).

Table S3. Comparisons of selected bond distances (Å) for $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot16H_2O$ (**1**), $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot16H_2O$ (**3**), $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot16H_2O$ (**4**), $[Mo_3O(OH)_3(Hnta)_3]Cl\cdot3H_2O$ (**5**),[1] $Mo_6O_{10}(bpy)_4(Hnta)_2$ (**6**),[2] $[Nd(H_2O)_8Mo_3O_3S(Hnta)_2(nta)]\cdot7H_2O$ (**7**),[3] $La_{0.75}Cl_{0.25}[Mo_3S_4(Hnta)_3]\cdot18H_2O$ (**8**),[4] $La_2Cl[Mo_3S_4(nta)_3]\cdot17H_2O$ (**9**),[5] $(NH_4)_4[cis\text{-}Mo_2O_4(nta)_2]\cdot7H_2O$ (**10**),[1] $Na[Mo_2O_3S(Hnta)_2]_2\cdot Eu(H_2O)_9\cdot3H_2O$ (**11**),[6] $Na\{(H_2O)_6Dy[Mo_2O_3S(Hnta)_2]_2\}\cdot7.5H_2O$ (**12**),[6] $KNa[Mo_2O_2S_2(Hnta)_2]\cdot7H_2O$ (**13**),[7] $K_6[Mo_2O_2S_2(nta)_2][Mo_2O_2S_2(ntaH)_2]\cdot4H_2O$ (**14**),[8] $Na_2[Mo_2O_3S(Hnta)_2]\cdot6H_2O$ (**15**),[3] $[Mg(H_2O)_6][Mo_2O_5(nta)_2]\cdot6H_2O$ (**16**),[9] $[LiK(H_2O)_2MoO_3nta]_n$ (**17**),[10] $[LiRb(H_2O)_2MoO_3nta]_n$ (**18**),[10] $[CsLi(H_2O)_2MoO_3nta]_n$ (**19**),[10] $[\{Fe(H_2O)_4\}\{Fe(NO)(nta)\}_2]_{n/n}\cdot2H_2O$ (**20**),[11] $(pyH)_2[Fe(nta)Cl_2]\cdot H_2O$ (**21**),[12] $Na_3[Fe(nta)_2]\cdot5H_2O$ (**22**),[13] $K_4[Fe_2(nta)_2(CO_3)O]\cdot2CH_3OH\cdot2H_2O$ (**23**),[14] $[Al(nta)(H_2O)_2]\cdot(CH_3)_2CO\cdot H_2O$ (**24**),[15] $[Al(H_2O)_2][Al_2(nta)_2(\mu\text{-}OH)_2][OH]\cdot3H_2O$ (**25**),[15] $[(Zn(nta)H_2O)_2(Al(nta)(\mu_2\text{-}OH)_2)_2(Al_{30}(\mu_2\text{-}OH)_{54}(\mu_3\text{-}OH)_6(\mu_4\text{-}O)_8(H_2O)_{20}(2,6\text{-}NDS)_5(H_2O)_{64}]$ (**26**),[16] $Cs[Cr(nta)_2]\cdot2H_2O$ (**27**),[17] $[Mg(H_2O)_6][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot4H_2O$ (**28**),[18] $[Ca(H_2O)_3][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot3H_2O$ (**29**),[18] $[Sr(H_2O)_3][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot3H_2O$ (**30**),[18] $[Ba(H_2O)_3\text{-}dmso][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot2H_2O$ (**31**),[18] $[Ba(H_2O)_4Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot3H_2O$ (**32**),[19] $[Zn(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot7H_2O$ (**33**),[19] $[Ni(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot7H_2O$ (**34**),[19] $[Co(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot7H_2O$ (**35**),[19] $[Mn(H_2O)_3(bpy)Cr_2(OH)_2(nta)_2]\cdot(bpy)\cdot5H_2O$ (**36**),[19] $[\{Cu(phen)_2\}_2\{Cr_2(\mu\text{-}OH)_2(nta)_2\}][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot8H_2O$ (**37**),[20] $[CaCr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2\cdot6H_2O]2H_2O$ (**38**),[21] $[Sr_2Cr_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2(nta)_4 7H_2O]14H_2O$ (**39**),[21]

$[Pb_2Cr_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2(nta)_4 7H_2O]14H_2O$ (**40**)[21] and $\{[Ag(\mu\text{-}H_2O)Ag(nta)Cr(\mu\text{-}OH)(\mu\text{-}AcO,O')Cr(nta)]\ H_2O\}_n$ (**41**)[22]

Table S4. Comparisons of selected bond distances (Å) for $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**), $[Fe(ida)(NO)(OH_2)_2]$ (**42**),[23] $[Fe(heida)(NO)(OH_2)]$ (**43**),[23] $[Fe(bnida)(NO)(OH_2)_2]$ (**44**),[23] $[Fe(NO)(OH_2)_2(phida)]\ H_2O$ (**45**),[23] $[Fe(brbnida)(NO)(OH_2)_2]$ (**46**),[23] $[Fe(dipic)(NO)(OH_2)_2]$ (**47**),[23] $[Fe(dipic)(H_2O)_3]$ (**48**),[23] $K[Fe(ida)_2]\ 3H_2O$ (**49**),[24] $(pyH)[Fe(ida)_2]$ (**50**),[12] $K_4[Fe_2O(ida)_4]\cdot 10H_2O$ (**51**)[25] and $[Fe_3L_2(ida)(\mu\text{-}OH)_3(\mu\text{-}O)]_2\ 4ClO_4\ 2CH_3OH\ 8H_2O$ (L = *N*-methyl-*N*,*N*-bis(2-pyridylmethyl)amine) (**52**)[26]

Table S5. Selected bond distances (Å) and angles (°) for $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**).

Table S6. Selected bond distances (Å) and angles (°) for $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**).

Table S7. Selected bond distances (Å) and angles (°) for $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**).

Table S8. Selected bond distances (Å) and angles (°) for $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

Table S9. Selected bond distances (Å) and angles (°) within the water layers in $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**).

Table S10. Selected bond distances (Å) and angles (°) within the water layers in $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

Figure S1. $[MoO_4]$ layers and [Fe(ida)] layers of $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *a* axis.

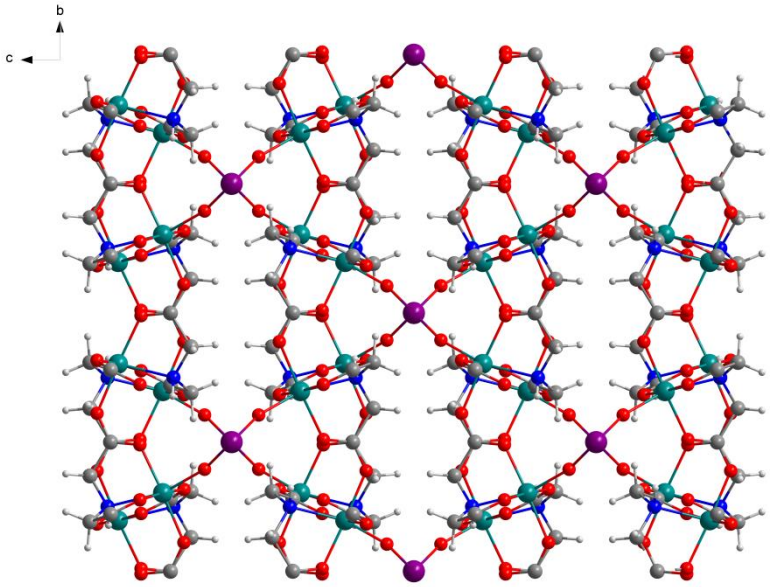

Figure S2. [Fe(ida)] layers of $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *c* axis.

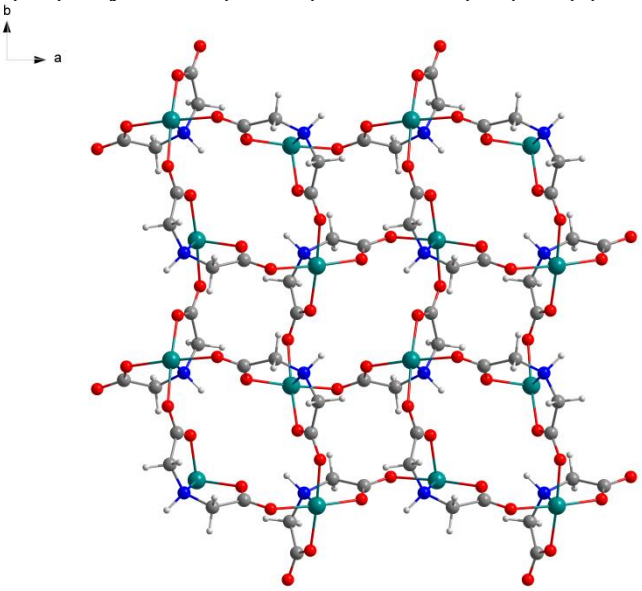

Figure S3. IR spectrum of $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**), $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**) and $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

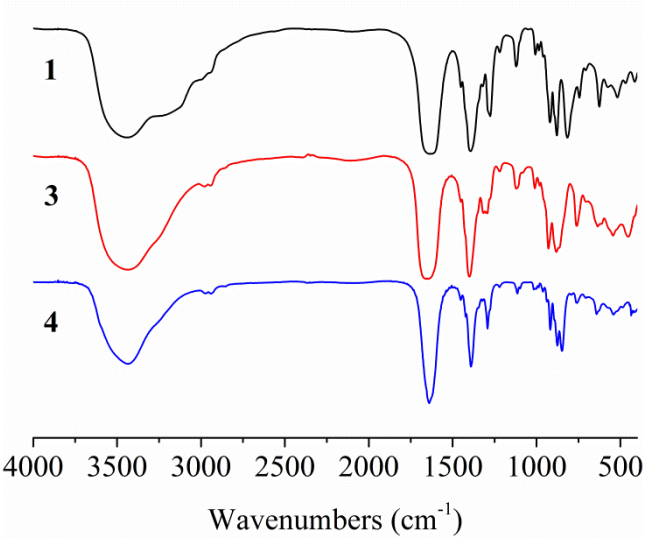

Figure S4. IR spectrum of $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**).

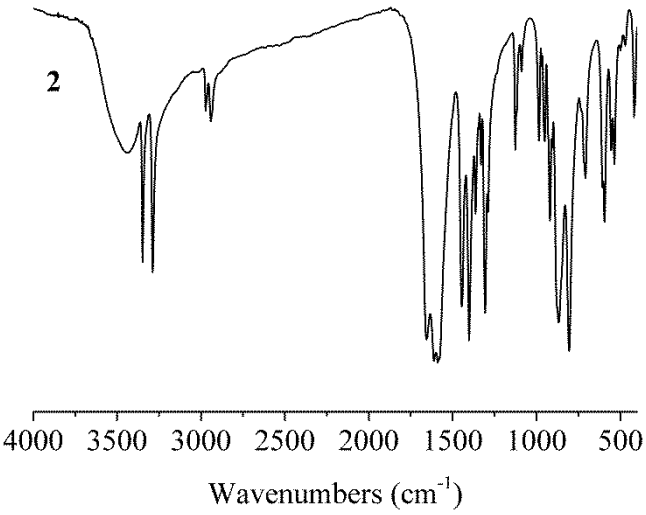

Figure S5. Solution UV-vis spectra of $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**), $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**) and $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

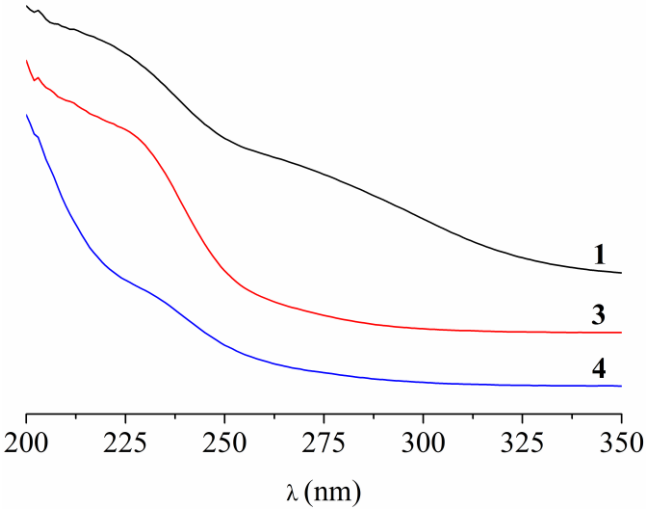

Figure S6. Solution UV-vis spectrum of $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**).

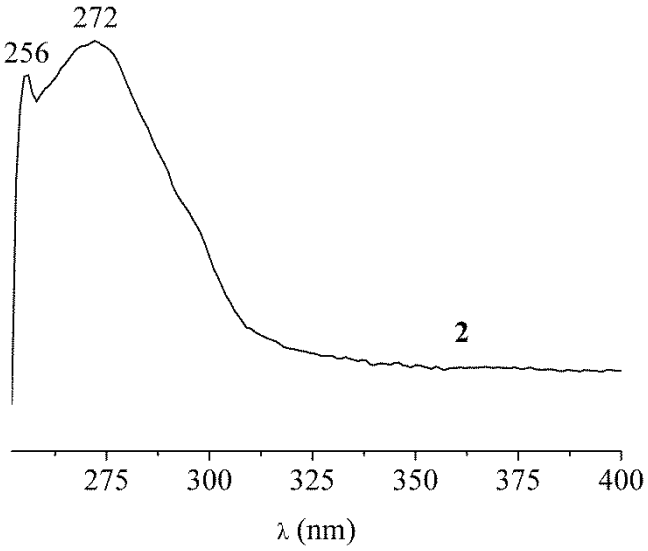

Figure S7. TG–DTG curves of $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**).

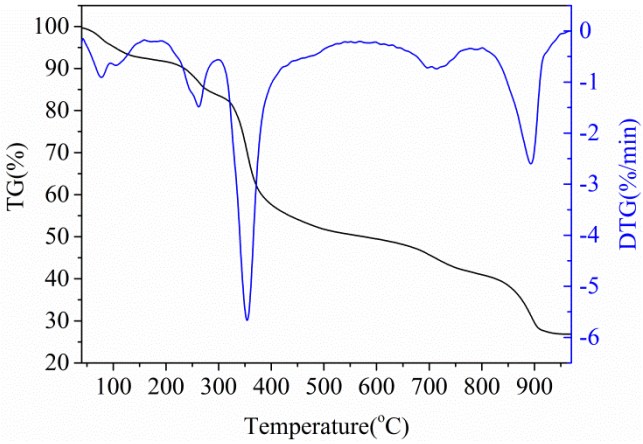

Figure S8. TG–DTG curves of $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**).

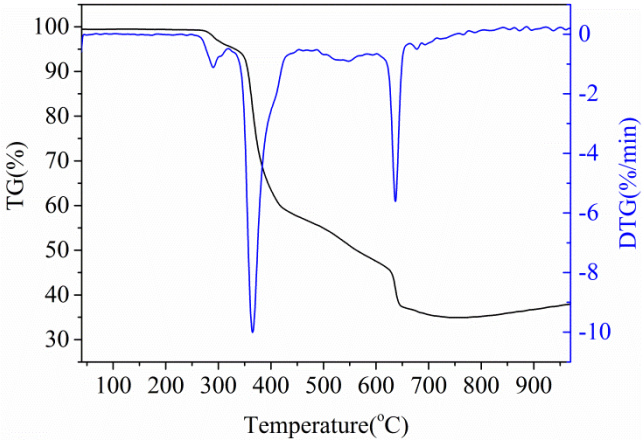

Figure S9. TG–DTG curves of $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**).

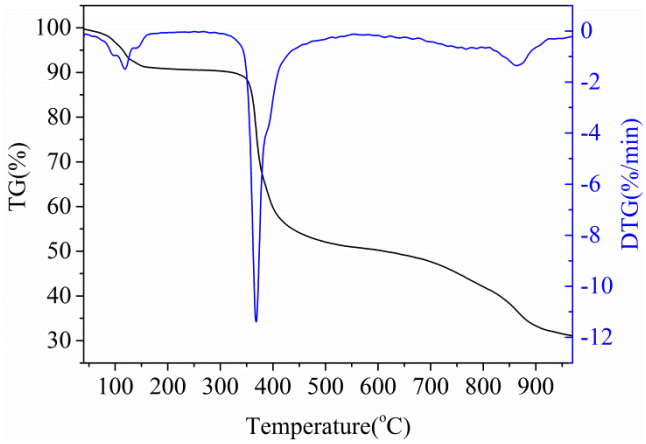

Figure S10. TG–DTG curves of $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

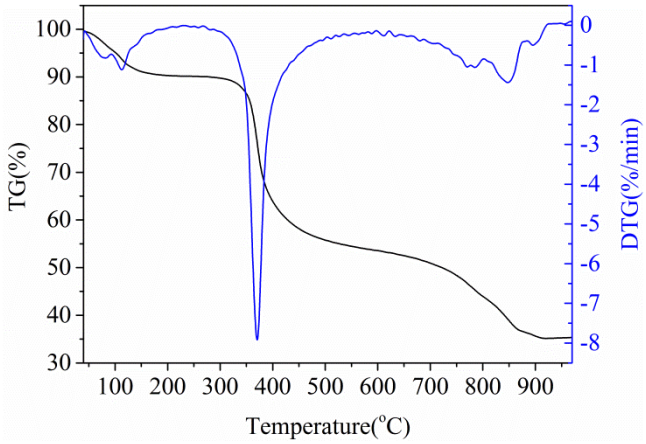

Figure S11. 2D layered structure of $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**).

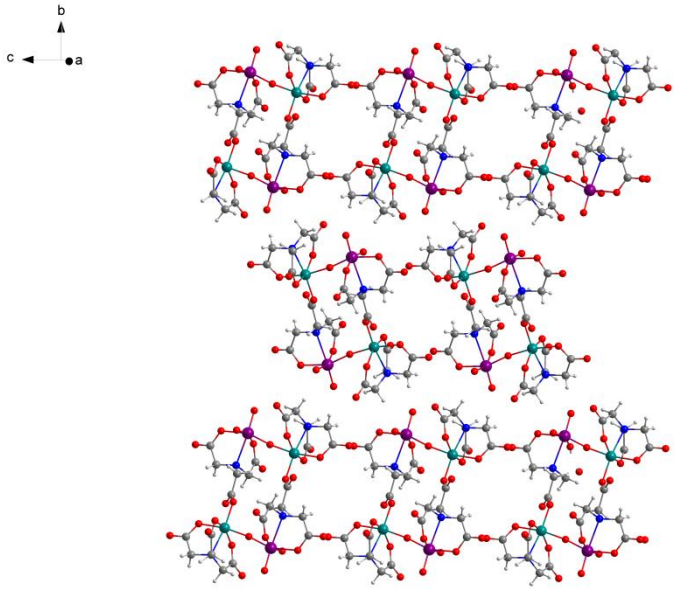

Figure S12. ORTEP plot of the molecular structure of $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**) at the 30% probability levels.

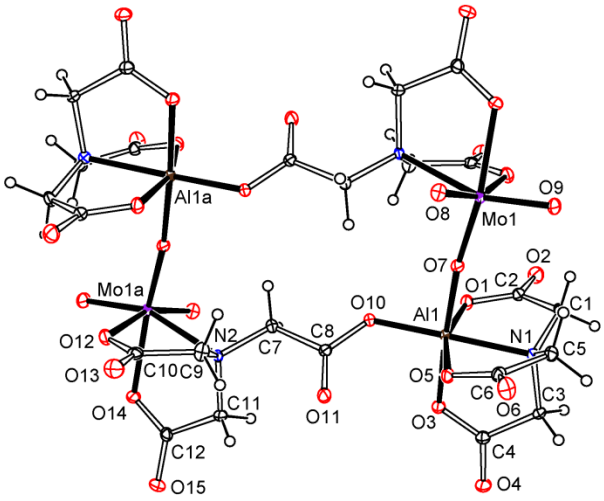

Figure S13. 2D layered structure of $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**) viewed along *b* axis.

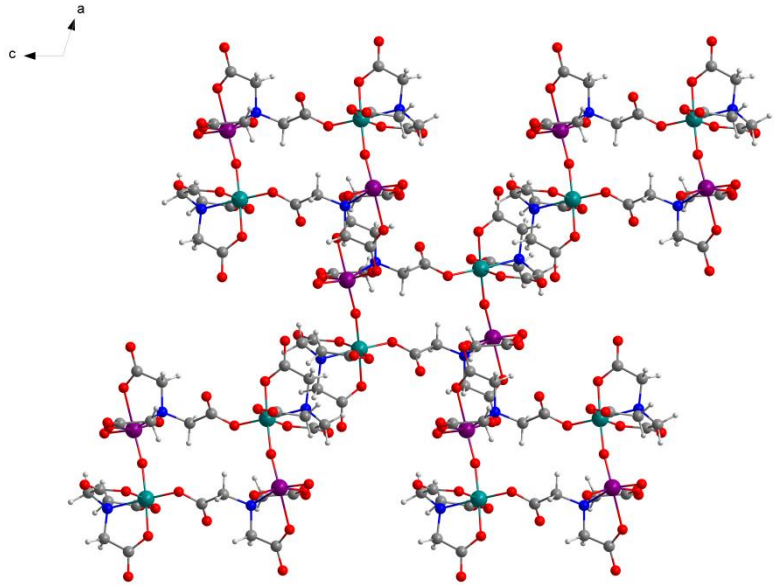

Figure S14. ORTEP plot of the molecular structure of $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**) at the 30% probability levels.

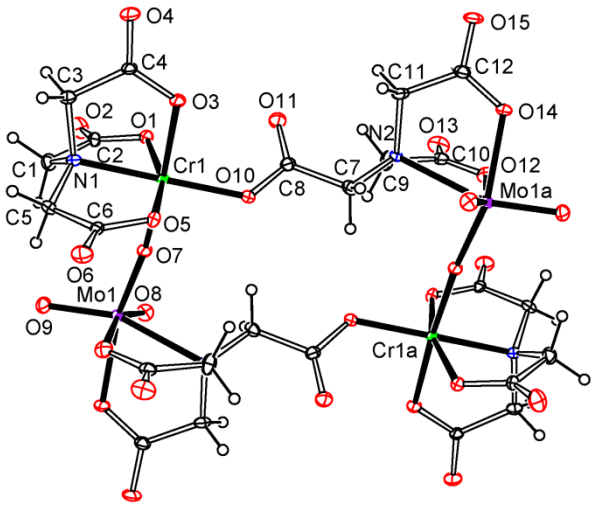

Figure S15. 2D layered structure of $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**) viewed along *b* axis.

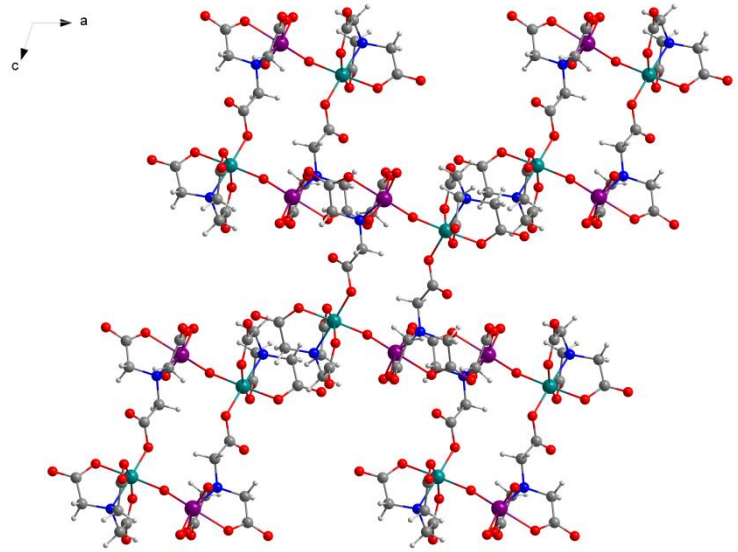

Figure S16. The coordination environment of Fe atoms in $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**).

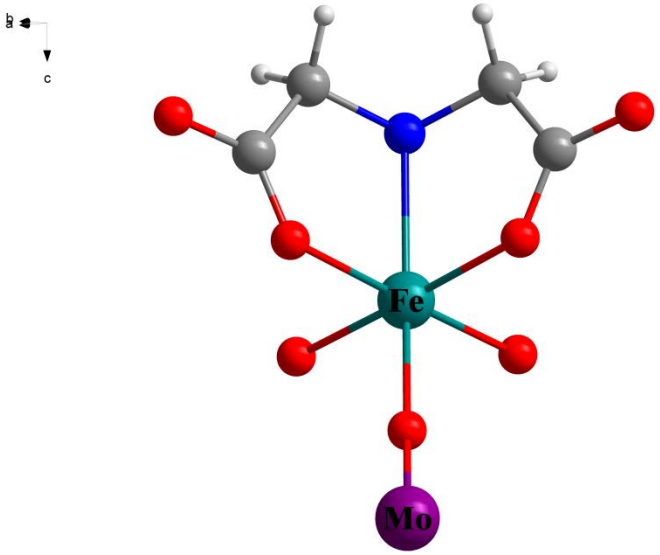

Figure S17. Schematic description of the equivalent topology framework with a 4,5-connected dinodalnbo-x-d/I m -3 m->I -4 2 m topological motif considering the MoO_4 and Fe-ida mononuclear units as connected nodes in $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *a* axis. Color codes: violet for MoO_4units 4-connected nodes, teal for Fe-ida mononuclear units 5-connected nodes.

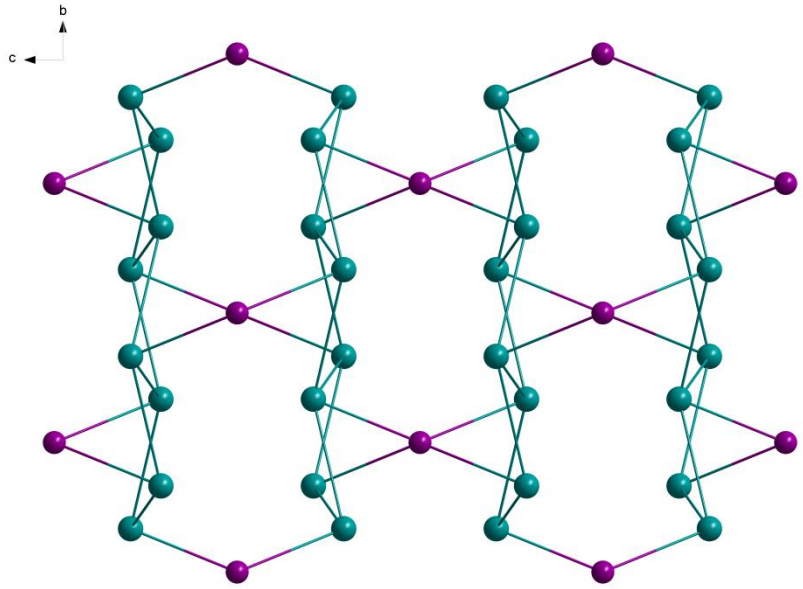

Figure S18. Schematic description of the equivalent topology framework with a 4,5-connected dinodalnbo-x-d/I m -3 m->I -4 2 m topological motif considering the MoO_4 and Fe-ida mononuclear units as connected nodes in $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *b*axis. Color codes: violet for MoO_4units 4-connected nodes, teal for Fe-ida mononuclear units 5-connected nodes.

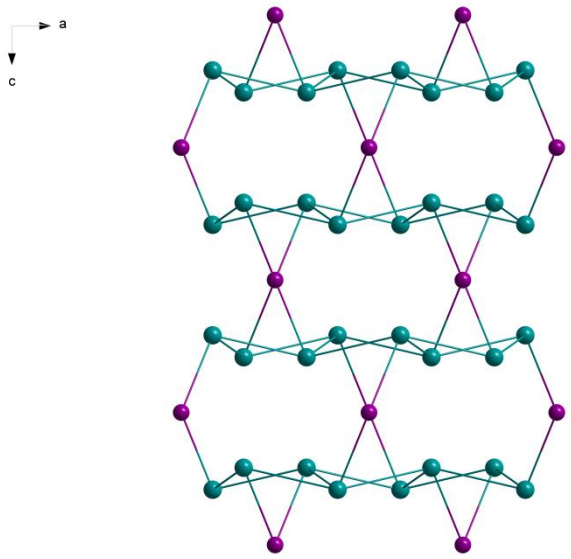

Figure S19. Schematic description of the equivalent topology framework with a 4,5-connected dinodalnbo-x-d/I m -3 m->I -4 2 m topological motif considering the MoO_4 and Fe-ida mononuclear units as connected nodes in $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**) viewed along *c* axis. Color codes: teal for MoO_4 units 4-connected nodes, yellow for Fe-ida mononuclear units 5-connected nodes.

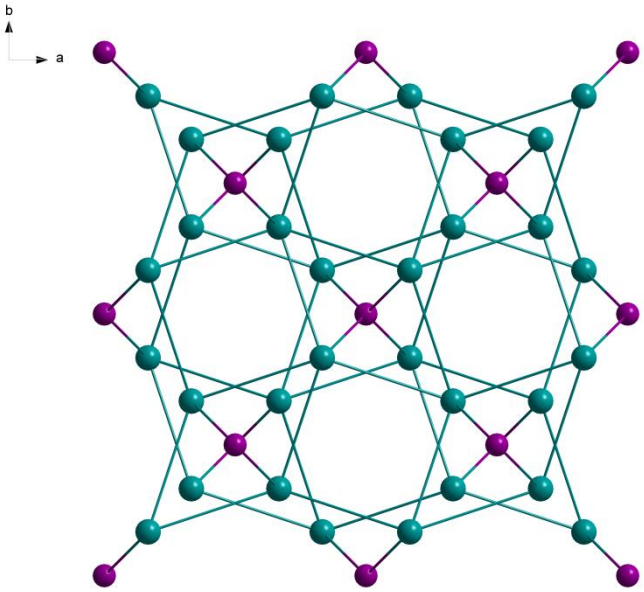

Table S1. Crystallographic data and structural refinements for complexes $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**), $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**), $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**) and $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

Identification code	**1**	**2**
Empirical formula	$C_{24}H_{56}Fe_2Mo_2N_4Na_6O_{46}$	$C_{32}H_{40}Fe_8Mo_2N_8O_{40}$
Formula weight	1578.24	1815.40
Temperature/K	173	173
Crystal system	monoclinic	tetragonal
Space group	$P\ 2_1/c$	I -42m
a/Å	10.5180(3)	9.7754(2)
b/Å	25.1402(5)	9.7754(2)
c/Å	11.0330(3)	13.7948(4)
α/°	90	90
β/°	110.479(3)	90
γ/°	90	90
Volume/Å^3	2733.0 (1)	1318.21(7)
Z	2	1
d_{calc}g/cm^3	1.908	2.287
μ/mm^{-1}	1.139	2.714
F(000)	1596.0	900.0
Crystal size/mm^3	0.4 ×0.2 ×0.1	0.2 ×0.1 ×0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/ °	6.26 to 59.97	5.108 to 59.808
Index ranges	-14 ≤ h ≤ 14, -34 ≤ k ≤ 31, -15 ≤ l ≤ 11	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -19 ≤ l ≤ 15
Reflections collected	13230	5335
Independent reflections	6869 [R_{int} = 0.0299, R_{sigma} = 0.0452]	950 [R_{int} = 0.0417, R_{sigma} = 0.0373]
Data/restraints/parameters	6869/9/409	950/0/57
Goodness–of–fit on F^2	1.022	1.335
Final R indexes [I≥2σ (I)]	R_1 = 0.0424, wR_2 = 0.1004	R_1 = 0.0600, wR_2 = 0.1379
Final R indexes [all data]	R_1 = 0.0488, wR_2 = 0.1042	R_1 = 0.0607, wR_2 = 0.1384
Largest diff. peak/hole / e ·Å^{-3}	3.41/-1.09	0.82/-1.56

Identification code	**3**	**4**
Empirical formula	$C_{24}H_{56}Al_2Mo_2N_4Na_6O_{46}$	$C_{24}H_{54}Cr_2Mo_2N_4Na_6O_{46}$
Formula weight	1520.48	1568.50
Temperature/K	173	173
Crystal system	monoclinic	monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$
a/Å	15.4271(4)	15.5265(7)
b/Å	11.0633(2)	11.0330(6)
c/Å	16.3607(3)	16.5498(10)
α/°	90	90
β/°	107.399(2)	107.693(6)
γ/°	90	90
Volume/Å^3	2664.59(10)	2700.9(3)
Z	2	2
d_{calc}g/cm^3	1.895	1.926
μ/mm^{-1}	0.678	1.017
F(000)	1544.0	1580.0
Crystal size/mm^3	0.4 ×0.4 ×0.2	0.4 ×0.4 ×0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/ °	4.512 to 59.756	4.506 to 59.692
Index ranges	-21 ≤ h ≤ 12, -15 ≤ k ≤ 14, -15 ≤ l ≤ 22	-13 ≤ h ≤ 21, -15 ≤ k ≤ 12, -21 ≤ l ≤ 12
Reflections collected	12903	13034
Independent reflections	6712 [R_{int} = 0.0264, R_{sigma} = 0.0422]	6786 [R_{int} = 0.0272, R_{sigma} = 0.0405]
Data/restraints/parameters	6712/7/413	6786/9/426
Goodness–of–fit on F^2	1.048	1.145
Final *R* indexes [I≥2σ (I)]	R_1 = 0.0513, wR_2 = 0.1283	R_1 = 0.0629, wR_2 = 0.1669
Final *R* indexes [all data]	R_1 = 0.0604, wR_2 = 0.1350	R_1 = 0.0715, wR_2 = 0.1725
Largest diff. peak/hole / e ·Å^{-3}	3.33/-2.25	2.15/-1.38

Table S2. Selected bond distances (Å) and angles (°) within the water layers in $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**).

D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O_{1w}–H ··O_{6a}	0.89	1.91	2.775(1)	164
O_{1w}–H ··O_{3w}	0.89	1.99	2.862(2)	168
O_{2w}–H ··O_{9b}	0.87	2.56	3.377(2)	156
O_{2w}–H ··O_{14c}	0.87	2.52	3.173(2)	133
O_{2w}–H ··O_{1w}	0.87	2.03	2.902(2)	175
O_{3w}–H ··O_{12d}	0.87	2.57	3.045(2)	115
O_{3w}–H ··O_{13d}	0.87	2.05	2.913(2)	170
O_{3w}–H ··O_{2we}	0.87	2.22	2.941(2)	140
O_{4w}–H ··O_{2f}	0.88	2.13	2.933(1)	150
O_{4w}–H ··O_{6w}	0.88	1.94	2.823(2)	174
O_{5w}–H ··O_{6a}	0.855(2)	2.175(1)	2.881(1)	139.8(2)
O_{5w}–H ··O_{7w}	0.855(1)	1.941(2)	2.785(2)	169.3(2)
O_{6w}–H ··O_{9b}	0.87	2.07	2.918(2)	165
O_{6w}–H ··O_{15g}	0.87	1.98	2.848(2)	172
O_{7w}–H ··O_{1f}	0.87	2.07	2.808(2)	142
O_{7w}–H ··O_{2wh}	0.87	2.07	2.925(2)	166
O_{8w}–H ··O_{13i}	0.848(3)	1.914(4)	2.760(1)	175.6(6)
O_{8w}–H ··O_{15j}	0.848(3)	2.007(4)	2.849(1)	172.5(3)

Symmetry codes: (a) -1 + *x*, *y*, *z*; (b) -1 + *x*, ½ – *y*, ½ + *z*; (c) -*x*, -½ + *y*, ½ – *z*; (d) -*x*, 1 – *y*, -*z*; (e) *x*, ½ – *y*, -½ + *z*; (f) *x*, *y*, 1 + *z*; (g) -*x*, 1 – *y*, 1 – *z*; (h) *x*, ½ – *y*, ½ + *z*; (i) 1 – *x*, 1 – *y*, -*z*; (j) 1 + *x*, *y*, *z*; (k) 1 – *x*, 1 – *y*, 1 – *z*.

Table S3. Comparisons of selected bond distances (Å) for $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**), $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**), $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**), $[Mo_3O(OH)_3(Hnta)_3]Cl\cdot 3H_2O$ (**5**),[1] $Mo_6O_{10}(bpy)_4(Hnta)_2$ (**6**),[2] $[Nd(H_2O)_8Mo_3O_3S(Hnta)_2(nta)]\cdot 7H_2O$ (**7**),[3] $La_{0.75}Cl_{0.25}[Mo_3S_4(Hnta)_3]\cdot 18H_2O$ (**8**),[4] $La_2Cl[Mo_3S_4(nta)_3]\cdot 17H_2O$ (**9**),[5] $(NH_4)_4[cis\text{-}Mo_2O_4(nta)_2]\cdot 7H_2O$ (**10**),[1] $Na[Mo_2O_3S(Hnta)_2]_2\cdot Eu(H_2O)_9\cdot 3H_2O$ (**11**),[6] $Na\{(H_2O)_6Dy[Mo_2O_3S(Hnta)_2]_2\}\cdot 7.5H_2O$ (**12**),[6] $KNa[Mo_2O_2S_2(Hnta)_2]\cdot 7H_2O$ (**13**),[7] $K_6[Mo_2O_2S_2(nta)_2][Mo_2O_2S_2(ntaH)_2]\cdot 4H_2O$ (**14**),[8] $Na_2[Mo_2O_3S(Hnta)_2]\cdot 6H_2O$ (**15**),[3] $[Mg(H_2O)_6][Mo_2O_5(nta)_2]\cdot 6H_2O$ (**16**),[9] $[LiK(H_2O)_2MoO_3nta]_n$ (**17**),[10] $[LiRb(H_2O)_2MoO_3nta]_n$ (**18**),[10] $[CsLi(H_2O)_2MoO_3nta]_n$ (**19**),[10] $[\{Fe(H_2O)_4\}\{Fe(NO)(nta)\}_2]_{n/n}\cdot 2H_2O$ (**20**),[11] $(pyH)_2[Fe(nta)Cl_2]\cdot H_2O$ (**21**),[12] $Na_3[Fe(nta)_2]\cdot 5H_2O$ (**22**),[13] $K_4[Fe_2(nta)_2(CO_3)O]\cdot 2CH_3OH\cdot 2H_2O$ (**23**),[14] $[Al(nta)(H_2O)_2]\cdot(CH_3)_2CO\cdot H_2O$ (**24**),[15] $[Al(H_2O)_2][Al_2(nta)_2(\mu\text{-}OH)_2][OH]\cdot 3H_2O$ (**25**),[15] $[(Zn(nta)H_2O)_2(Al(nta)(\mu_2\text{-}OH)_2)_2(Al_{30}(\mu_2\text{-}OH)_{54}(\mu_3\text{-}OH)_6(\mu_4\text{-}O)_8(H_2O)_{20}(2,6\text{-}NDS)_5(H_2O)_{64}]$ (**26**),[16] $Cs[Cr(nta)_2]\cdot 2H_2O$ (**27**),[17] $[Mg(H_2O)_6][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 4H_2O$ (**28**),[18] $[Ca(H_2O)_3][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 3H_2O$ (**29**),[18] $[Sr(H_2O)_3][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 3H_2O$ (**30**),[18] $[Ba(H_2O)_3\text{-}dmso][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 2H_2O$ (**31**),[18] $[Ba(H_2O)_4Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 3H_2O$ (**32**),[19] $[Zn(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot 7H_2O$ (**33**),[19] $[Ni(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot 7H_2O$ (**34**),[19] $[Co(bpy)_2(H_2O)_2][Cr_2(OH)_2(nta)_2]\cdot 7H_2O$ (**35**),[19] $[Mn(H_2O)_3(bpy)Cr_2(OH)_2(nta)_2]\cdot(bpy)\cdot 5H_2O$ (**36**),[19] $[\{Cu(phen)_2\}_2\{Cr_2(\mu\text{-}OH)_2(nta)_2\}][Cr_2(\mu\text{-}OH)_2(nta)_2]\cdot 8H_2O$ (**37**),[20] $[CaCr_2(\mu\text{-}OH)(\mu\text{-}OAc)(nta)_2\cdot 6H_2O]2H_2O$ (**38**),[21] $[Sr_2Cr_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2(nta)_4 7H_2O]14H_2O$ (**39**),[21] $[Pb_2Cr_4(\mu\text{-}OH)_2(\mu\text{-}OAc)_2(nta)_4 7H_2O]14H_2O$ (**40**)[21] and $\{[Ag(\mu\text{-}H_2O)Ag(nta)Cr(\mu\text{-}OH)(\mu\text{-}AcO,O')Cr(nta)]\cdot H_2O\}_n$ (**41**)[22]

Complexes(M^{n+})	M–$O_{\beta\text{-carboxy}}$	M–N	M–μ_2-O/S
1(Mo^{6+}/Fe^{3+})	2.152(1)$_{av}$(Mo)	2.375(1)(Mo)	1.794(1)(Mo)
	2.014(1)$_{av}$(Fe)	2.190(1)(Fe)	1.948(1)(Fe)
3(Mo^{6+}/Al^{3+})	2.167(1)$_{av}$(Mo)	2.376(1)(Mo)	1.787(1)(Mo)
	1.904(1)$_{av}$(Al)	2.080(1)(Al)	1.857(1)(Al)
4(Mo^{6+}/Cr^{3+})	2.171(1)$_{av}$(Mo)	2.379(1)(Mo)	1.788(1)(Mo)
	1.986(1)$_{av}$(Cr)	2.058(1)(Cr)	1.937(1)(Cr)
5[1](Mo^{4+})	2.082(9)$_{av}$	2.23(1)$_{av}$	1.903(8)$_{av}$
6[2](Mo^{4+})	2.130(4)$_{av}$	2.286(4)	1.935(3)$_{av}$
7[3](Mo^{4+})	2.100(4)$_{av}$	2.259(5)$_{av}$	1.925(4)$_{av}$
8[4](Mo^{4+})	2.114(6)$_{av}$	2.319(6)$_{av}$	2.302(2)$_{av}$
9[5](Mo^{4+})	2.135(2)$_{av}$	2.310(3)$_{av}$	2.290(1)$_{av}$
10[1](Mo^{5+})	2.125(3)$_{av}$	2.276(3)	1.930(3)$_{av}$
11[6](Mo^{5+})	2.163(5)$_{av}$	2.296(5)$_{av}$	1.920(4)$_{av}$/ 2.327(2)$_{av}$
12[6](Mo^{5+})	2.167(6)$_{av}$	2.302(6)$_{av}$	1.917(5)$_{av}$/

			$2.331(2)_{av}$
13[7](Mo^{5+})	$2.147(6)_{av}$	$2.346(5)_{av}$	$2.318(2)_{av}$
14[8](Mo^{5+})	$2.135(5)_{av}$	$2.316(5)_{av}$	$2.240(4)_{av}$
15[3](Mo^{5+})	$2.157(2)_{av}$	2.288(2)	1.923(2)/2.337(1)
16[9](Mo^{6+})	$2.124(2)_{av}$	2.418(2)	1.880(1)
17[10](Mo^{6+})	$2.194(3)_{av}$	2.407(3)	
18[10](Mo^{6+})	$2.192(2)_{av}$	2.407(2)	
19[10](Mo^{6+})	$2.188(3)_{av}$	2.413(3)	
20[11](Fe^{2+})	$2.071(2)_{av}$	2.226(3)	
21[12](Fe^{3+})	$2.008(1)_{av}$	2.236(1)	
22[13](Fe^{3+})	$2.050(2)_{av}$	$2.303(3)_{av}$	
23[14](Fe^{3+})	$2.042(3)_{av}$	2.246(4)	1.830(2)
24[15](Al^{3+})	$1.881(3)_{av}$	2.086(4)	
25[15](Al^{3+})	$1.901(2)_{av}$	2.073(3)	
26[16](Al^{3+})	$1.903(3)_{av}$	2.113(3)	$1.883(3)_{av}$
27[17](Cr^{3+})	$1.955(2)_{av}$	$2.091(2)_{av}$	
28[18](Cr^{3+})	$1.980(1)_{av}$	2.060(1)	$1.973(1)_{av}$
29[18](Cr^{3+})	$1.988(2)_{av}$	$2.067(2)_{av}$	$1.952(2)_{av}$
30[18](Cr^{3+})	$1.980(2)_{av}$	$2.064(3)_{av}$	$1.949(3)_{av}$
31[18](Cr^{3+})	$1.972(2)_{av}$	$2.055(3)_{av}$	$1.958(2)_{av}$
32[19](Cr^{3+})	$1.928(4)_{av}$	$2.069(5)_{av}$	$1.891(4)_{av}$
33[19](Cr^{3+})	$1.975(3)_{av}$	$2.071(3)_{av}$	$1.961(3)_{av}$
34[19](Cr^{3+})	$1.972(3)_{av}$	$2.061(3)_{av}$	$1.955(3)_{av}$
35[19](Cr^{3+})	$1.969(2)_{av}$	$2.061(2)_{av}$	$1.955(2)_{av}$
36[19](Cr^{3+})	$1.980(2)_{av}$	$2.069(2)_{av}$	$1.957(2)_{av}$
37[20](Cr^{3+})	$1.978(2)_{av}$	$2.069(2)_{av}$	$1.964(2)_{av}$
38[21](Cr^{3+})	$1.971(1)_{av}$	$2.068(1)_{av}$	$1.940(1)_{av}$
39[21](Cr^{3+})	$1.971(2)_{av}$	$2.068(2)_{av}$	$1.926(2)_{av}$
40[21](Cr^{3+})	$1.967(2)_{av}$	$2.069(3)_{av}$	$1.921(3)_{av}$
41[22](Cr^{3+})	$1.963(4)_{av}$	$2.065(4)_{av}$	$1.940(4)_{av}$

Table S4. Comparisons of selected bond distances (Å) for $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**), [Fe(ida)(NO)$(OH_2)_2$] (**42**),[23] [Fe(heida)(NO)(OH_2)] (**43**),[23] [Fe(bnida)(NO)$(OH_2)_2$] (**44**),[23] [Fe(NO)$(OH_2)_2$(phida)] ·H_2O (**45**),[23] [Fe(brbnida)(NO)$(OH_2)_2$] (**46**),[23] [Fe(dipic)(NO)$(OH_2)_2$] (**47**),[23] [Fe(dipic)$(H_2O)_3$] (**48**),[23] K[Fe(ida)$_2$] $3H_2O$ (**49**),[24] (pyH)[Fe(ida)$_2$] (**50**),[12] $K_4[Fe_2O(ida)_4]$ ·$10H_2O$ (**51**)[25] and $[Fe_3L_2(ida)(\mu\text{-}OH)_3(\mu\text{-}O)]_2$ ·$4ClO_4$ $2CH_3OH$ $8H_2O$ (L = *N*-methyl-*N*,*N*-bis(2-pyridylmethyl)amine) (**52**)[26]

Complexes (M^{n+})	$M–O_{\beta\text{-carboxy}}$	M–N
2($Fe^{2+/3+}$)	2.04(1)	2.22(1)
42[23](Fe^{2+})	2.051(3)	2.269(5)
43[23](Fe^{2+})	$2.055(2)_{av}$	2.224(3)
44[23](Fe^{2+})	$2.057(3)_{av}$	2.297(2)
45[23](Fe^{2+})	$2.026(1)_{av}$	2.320(2)
46[23](Fe^{2+})	$2.046(4)_{av}$	2.331(3)
47[23](Fe^{2+})	$2.121(2)_{av}$	$2.088(2)_{av}$
48[23](Fe^{2+})	$2.163(1)_{av}$	$2.082(1)_{av}$
49[24](Fe^{3+})	$1.976(3)_{av}$	$2.149(3)_{av}$
50[12](Fe^{3+})	$1.982(2)_{av}$	2.161(3)
51[25](Fe^{3+})	$2.046(3)_{av}$	$2.236(3)_{av}$
52[26](Fe^{3+})	$2.031(4)_{av}$	2.208(4)

Table S5. Selected bond distances (Å) and angles (°) for $Na_6[(MoO_2)_2O_2Fe_2(nta)_4]\cdot 16H_2O$ (**1**).

Mo(1)–O(7)	1.794(1)	Mo(1a)–N(2)	2.375(1)
Mo(1)–O(8)	1.7150(8)	Fe(1)–O(1)	2.0276(9)
Mo(1)–O(9)	1.7317(9)	Fe(1)–O(3)	2.000(1)
Mo(1)–O(12a)	2.1776(9)	Fe(1)–O(5)	2.0148(8)
Mo(1)–O(14a)	2.127(1)	Fe(1)–O(7)	1.948(1)
Mo(1)–N(2a)	2.375(1)	Fe(1)–O(10)	1.9530(9)
Mo(1a)–O(12)	2.1777(9)	Fe(1)–N(1)	2.190(1)
Mo(1a)–O(14)	2.127(1)		
O(7)–Mo(1)–O(8)	103.32(4)	O(3)–Fe(1)–O(10)	92.74(4)
O(7)–Mo(1)–O(9)	106.60(4)	O(3)–Fe(1)–N(1)	81.17(4)
O(7)–Mo(1)–O(12a)	86.00(4)	O(5)–Fe(1)–O(7)	90.23(4)
O(7)–Mo(1)–O(14a)	155.36(4)	O(5)–Fe(1)–O(10)	94.23(3)
O(7)–Mo(1)–N(2a)	84.46(4)	O(5)–Fe(1)–N(1)	79.47(3)
O(8)–Mo(1)–O(9)	106.60(4)	O(7)–Fe(1)–O(10)	96.97(4)
O(8)–Mo(1)–O(12a)	158.68(4)	O(7)–Fe(1)–N(1)	89.32(4)
O(8)–Mo(1)–O(14a)	89.46(4)	O(10)–Fe(1)–N(1)	171.15(4)
O(8)–Mo(1)–N(2a)	89.65(4)	Mo(1)–O(7)–Fe(1)	168.31(5)
O(9)–Mo(1)–O(12a)	88.77(4)	C(7)–N(2)–Mo(1a)	108.35(7)
O(9)–Mo(1)–O(14a)	90.21(4)	C(9)–N(2)–Mo(1a)	104.66(7)
O(9)–Mo(1)–N(2a)	157.75(4)	C(10)–O(12)–Mo(1a)	119.21(8)
O(12a)–Mo(1)–O(14a)	75.51(4)	C(11)–N(2)–Mo(1a)	109.32(7)
O(12a)–Mo(1)–N(2a)	71.98(3)	C(12)–O(14)–Mo(1a)	123.02(9)
O(14a)–Mo(1)–N(2a)	74.51(4)	C(1)–N(1)–Fe(1)	105.74(6)
O(1)–Fe(1)–O(3)	90.27(4)	C(2)–O(1)–Fe(1)	115.99(7)
O(1)–Fe(1)–O(5)	157.26(3)	C(3)–N(1)–Fe(1)	107.66(7)
O(1)–Fe(1)–O(7)	85.41(4)	C(4)–O(3)–Fe(1)	119.66(9)
O(1)–Fe(1)–O(10)	108.45(4)	C(5)–N(1)–Fe(1)	104.48(7)
O(1)–Fe(1)–N(1)	78.17(3)	C(6)–O(5)–Fe(1)	117.01(7)
O(3)–Fe(1)–O(5)	90.38(4)	C(8)–O(10)–Fe(1)	122.12(9)
O(3)–Fe(1)–O(7)	170.20(4)		

Symmetry codes: (a) $1 - x$, $1 - y$, $-z$.

Table S6. Selected bond distances (Å) and angles (°) for $[(MoO_4)_2Fe^{II}_4Fe^{III}_4(ida)_8]_n$ (**2**).

Mo(1)–O(3)	1.78(1)	Fe(1)–O(2e)	2.04(1)
Mo(1)–O(3a)	1.78(1)	Fe(1)–O(2f)	2.04(1)
Mo(1)–O(3b)	1.78(1)	Fe(1)–O(3)	2.03(1)
Mo(1)–O(3c)	1.78(1)	Fe(1)–N(1e)	2.22(1)
Fe(1)–O(1)	2.043(9)	Fe(1g)–O(2)	2.04(1)
Fe(1)–O(1d)	2.043(9)	Fe(1g)–N(1)	2.22(1)
O(3)–Mo(1)–O(3a)	109.4(3)	O(1)–Fe(1)–N(1f)	99.8(4)
O(3)–Mo(1)–O(3b)	109.4(3)	O(1d)–Fe(1)–N(1f)	99.8(4)
O(3)–Mo(1)–O(3c)	109.7(7)	O(2e)–Fe(1)–O(2f)	92.8(6)
O(3a)–Mo(1)–O(3b)	109.7(7)	O(2e)–Fe(1)–O(3)	89.6(3)
O(3a)–Mo(1)–O(3b)	109.4(3)	O(2f)–Fe(1)–O(3)	89.6(3)
O(3b)–Mo(1)–O(3c)	109.4(3)	O(2e)–Fe(1)–N(1f)	77.1(3)
O(1)–Fe(1)–O(1d)	88.2(6)	O(2f)–Fe(1)–N(1f)	77.1(3)
O(1)–Fe(1)–O(2e)	175.7(4)	O(3)–Fe(1)–N(1f)	160.5(5)
O(1)–Fe(1)–O(2f)	89.4(4)	Mo(1)–O(3)–Fe(1)	163.9(6)
O(1d)–Fe(1)–O(2e)	89.4(4)	C(1)–N(1)–Fe(1g)	109.8(6)
O(1d)–Fe(1)–O(2f)	175.7(4)	C(1h)–N(1)–Fe(1g)	109.8(6)
O(1)–Fe(1)–O(3)	94.2(3)	C(2)–O(1)–Fe(1)	128.1(7)
O(1d)–Fe(1)–O(3)	94.2(3)	C(2)–O(2)–Fe(1g)	120.7(9)

Symmetry codes: (a) -*y*, *x*, 1 – *z*; (b) *y*, -*x*, 1 – *z*; (c) -*x*, -*y*, *z*; (d) *y*, *x*, *z*; (e) ½ – *y*, -½ + *x*, 1½ – *z*; (f) -½ + *x*, ½ – *y*, 1½ – *z*; (g) ½ + *y*, ½ – *x*, 1½ – *z*; (h) 1 – *y*, 1 – *x*, *z*.

Table S7. Selected bond distances (Å) and angles (°) for $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**).

Mo(1)–O(7)	1.7874(9)	Mo(1a)–N(2)	2.376(1)
Mo(1)–O(8)	1.717(1)	Al(1)–O(1)	1.898(1)
Mo(1)–O(9)	1.732(1)	Al(1)–O(3)	1.890(1)
Mo(1)–O(12a)	2.208(1)	Al(1)–O(5)	1.923(1)
Mo(1)–O(14a)	2.1266(9)	Al(1)–O(7)	1.857(1)
Mo(1)–N(2a)	2.376(1)	Al(1)–O(10)	1.835(1)
Mo(1a)–O(12)	2.208(1)	Al(1)–N(1)	2.080(1)
Mo(1a)–O(14)	2.1266(9)		
O(7)–Mo(1)–O(8)	103.70(5)	O(3)–Al(1)–O(10)	91.59(5)
O(7)–Mo(1)–O(9)	105.49(5)	O(3)–Al(1)–N(1)	85.24(5)
O(7)–Mo(1)–O(12a)	85.83(4)	O(5)–Al(1)–O(7)	87.60(5)
O(7)–Mo(1)–O(14a)	156.97(5)	O(5)–Al(1)–O(10)	104.22(5)
O(7)–Mo(1)–N(2a)	88.93(4)	O(5)–Al(1)–N(1)	80.59(5)
O(8)–Mo(1)–O(9)	105.61(5)	O(7)–Al(1)–O(10)	92.63(5)
O(8)–Mo(1)–O(12a)	158.11(5)	O(7)–Al(1)–N(1)	90.75(5)
O(8)–Mo(1)–O(14a)	90.69(5)	O(10)–Al(1)–N(1)	174.22(6)
O(8)–Mo(1)–N(2a)	87.62(5)	Mo(1)–O(7)–Al(1)	172.46(7)
O(9)–Mo(1)–O(12a)	90.33(5)	C(7)–N(2)–Mo(1a)	107.83(8)
O(9)–Mo(1)–O(14a)	87.36(5)	C(9)–N(2)–Mo(1a)	107.08(9)
O(9)–Mo(1)–N(2a)	157.06(4)	C(10)–O(12)–Mo(1a)	121.6(1)
O(12a)–Mo(1)–O(14a)	74.87(4)	C(11)–N(2)–Mo(1a)	108.32(8)
O(12a)–Mo(1)–N(2a)	72.70(4)	C(12)–O(14)–Mo(1a)	123.51(8)
O(14a)–Mo(1)–N(2a)	73.58(4)	C(1)–N(1)–Al(1)	105.43(9)
O(1)–Al(1)–O(3)	90.65(5)	C(2)–O(1)–Al(1)	118.4(1)
O(1)–Al(1)–O(5)	162.75(5)	C(3)–N(1)–Al(1)	106.52(8)
O(1)–Al(1)–O(7)	91.40(5)	C(4)–O(3)–Al(1)	117.98(9)
O(1)–Al(1)–O(10)	93.03(5)	C(5)–N(1)–Al(1)	105.54(9)
O(1)–Al(1)–N(1)	82.20(5)	C(6)–O(5)–Al(1)	115.96(9)
O(3)–Al(1)–O(5)	89.16(5)	C(8)–O(10)–Al(1)	128.9(1)
O(3)–Al(1)–O(7)	175.21(5)		

Symmetry codes: (a) $1 - x$, $1 - y$, $1 - z$.

Table S8. Selected bond distances (Å) and angles (°) for $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

Mo(1)–O(7)	1.788(1)	Mo(1a)–N(2)	2.379(2)
Mo(1)–O(8)	1.730(2)	Cr(1)–O(1)	2.009(2)
Mo(1)–O(9)	1.741(2)	Cr(1)–O(3)	1.969(1)
Mo(1)–O(12a)	2.216(2)	Cr(1)–O(5)	1.981(2)
Mo(1)–O(14a)	2.126(1)	Cr(1)–O(7)	1.937(1)
Mo(1)–N(2a)	2.379(2)	Cr(1)–O(10)	1.967(2)
Mo(1a)–O(12)	2.216(2)	Cr(1)–N(1)	2.058(2)
Mo(1a)–O(14)	2.126(1)		
O(7)–Mo(1)–O(8)	103.67(7)	O(3)–Cr(1)–O(10)	91.44(6)
O(7)–Mo(1)–O(9)	105.11(7)	O(3)–Cr(1)–N(1)	85.20(6)
O(7)–Mo(1)–O(12a)	85.38(6)	O(5)–Cr(1)–O(7)	92.47(6)
O(7)–Mo(1)–O(14a)	156.68(6)	O(5)–Cr(1)–O(10)	91.62(6)
O(7)–Mo(1)–N(2a)	88.54(6)	O(5)–Cr(1)–N(1)	82.73(7)
O(8)–Mo(1)–O(9)	106.24(8)	O(7)–Cr(1)–O(10)	91.92(6)
O(8)–Mo(1)–O(12a)	158.21(7)	O(7)–Cr(1)–N(1)	91.73(6)
O(8)–Mo(1)–O(14a)	90.51(6)	O(10)–Cr(1)–N(1)	173.40(7)
O(8)–Mo(1)–N(2a)	87.48(7)	Mo(1)–O(7)–Cr(1)	170.04(9)
O(9)–Mo(1)–O(12a)	90.01(7)	C(7)–N(2)–Mo(1a)	107.1(1)
O(9)–Mo(1)–O(14a)	88.11(6)	C(9)–N(2)–Mo(1a)	107.5(1)
O(9)–Mo(1)–N(2a)	157.29(6)	C(10)–O(12)–Mo(1a)	121.8(1)
O(12a)–Mo(1)–O(14a)	75.32(6)	C(11)–N(2)–Mo(1a)	108.0(1)
O(12a)–Mo(1)–N(2a)	72.79(6)	C(12)–O(14)–Mo(1a)	123.5(1)
O(14a)–Mo(1)–N(2a)	73.47(5)	C(1)–N(1)–Cr(1)	106.0(1)
O(1)–Cr(1)–O(3)	89.04(6)	C(2)–O(1)–Cr(1)	114.3(1)
O(1)–Cr(1)–O(5)	163.04(6)	C(3)–N(1)–Cr(1)	107.7(1)
O(1)–Cr(1)–O(7)	87.45(6)	C(4)–O(3)–Cr(1)	115.7(1)
O(1)–Cr(1)–O(10)	105.33(6)	C(5)–N(1)–Cr(1)	105.7(1)
O(1)–Cr(1)–N(1)	80.33(6)	C(6)–O(5)–Cr(1)	115.2(1)
O(3)–Cr(1)–O(5)	90.16(6)	C(8)–O(10)–Cr(1)	125.9(1)
O(3)–Cr(1)–O(7)	175.68(7)		

Symmetry codes: (a) $1 - x$, $1 - y$, $1 - z$.

Table S9. Selected bond distances (Å) and angles (°) within the water layers in $Na_6[(MoO_2)_2O_2Al_2(nta)_4]\cdot 16H_2O$ (**3**).

D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O_{1w}–H ··O_{3a}	0.849(2)	2.368(1)	3.173(2)	158.5(1)
O_{1w}–H ··O_{9b}	0.851(1)	2.055(2)	2.887(2)	165.8(1)
O_{1w}–H ··O_{11a}	0.849(2)	2.592(2)	3.097(2)	119.3(1)
O_{2w}–H ··O_{3w}	0.848(3)	1.887(3)	2.709(2)	162.9(2)
O_{2w}–H ··O_{5wa}	0.849(3)	2.043(3)	2.864(2)	162.4(2)
O_{3w}–H ··O_{13c}	0.85	2.51	2.809(2)	101
O_{3w}–H ··O_{4wd}	0.85	2.55	2.871(3)	103
O_{3w}–H ··O_{7we}	0.85	2.21	2.843(5)	132
O_{4w}–H ··O_{6}	0.93	1.94	2.721(2)	140
O_{4w}–H ··O_{3wf}	0.93	1.98	2.871(3)	159
O_{5w}–H ··O_{2g}	0.89	2.00	2.782(2)	145
O_{5w}–H ··O_{12h}	0.89	2.52	3.010(2)	115
O_{6w}–H ··O_{6i}	0.90	2.12	2.786(2)	130
O_{6w}–H ··O_{7w}	0.90	1.97	2.764(3)	146
O_{7w}–H ··O_{1e}	0.85	2.49	2.976(2)	117
O_{7w}–H ··O_{3we}	0.85	2.44	2.843(5)	110
O_{7w}–H ··O_{6w}	0.85	2.43	2.764(3)	104
O_{8w}–H ··O_{4wc}	0.85	1.67	2.429(2)	147

Symmetry codes: (a) -*x*, 1 – *y*, 1 – *z*; (b) ½ – *x*, -½ + *y*, 1½ – *z*; (c) ½ – *x*, -½ + *y*, ½ – *z*; (d) *x*, -1+ *y*, *z*; (e) 1 – *x*, 1 – *y*, 1 – *z*; (f) *x*, 1 + *y*, *z*; (g) ½ – *x*, ½ + *y*, 1½ – *z*; (h) ½ – *x*, ½ + *y*, ½ – *z*; (i) 1 – *x*, 2 – *y*, 1 – *z*.

Table S10. Selected bond distances (Å) and angles (°) within the water layers in $Na_6[(MoO_2)_2O_2Cr_2(nta)_4]\cdot 16H_2O$ (**4**).

D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O_{1w}–H ··O_2	0.95	1.99	2.775(3)	138
O_{1w}–H ··O_{8wa}	0.95	2.05	2.885(5)	145
O_{2w}–H ··O_{12b}	0.91	2.49	2.990(2)	115
O_{2w}–H ··O_{4wc}	0.91	2.06	2.879(3)	149
O_{3w}–H ··O_{3c}	0.861(2)	2.285(2)	3.138(2)	171.2(2)
O_{3w}–H ··O_{9d}	0.854(2)	2.021(2)	2.870(2)	172.9(2)
O_{4w}–H ··O_{2wc}	0.849(3)	2.078(4)	2.879(3)	157.2(1)
O_{4w}–H ··O_{8w}	0.846(3)	2.039(4)	2.680(4)	132.0(2)
O_{5w}–H ··O_{2e}	0.93	2.00	2.840(3)	149
O_{5w}–H ··O_{15b}	0.93	1.82	2.722(2)	162
O_{7w}–H ··O_{5f}	0.85	2.51	3.122(3)	130
O_{7w}–H ··O_{10f}	0.85	2.14	2.920(4)	152
O_{7w}–H ··O_{8wf}	0.85	2.22	2.941(6)	143
O_{8w}–H ··O_{1wg}	0.85	2.09	2.885(5)	157
O_{8w}–H ··O_{7wf}	0.85	2.53	2.941(6)	111

Symmetry codes: (a) *x*, -1 + *y*, *z*; (b) 1½ – *x*, -½ + *y*, 1½ – *z*; (c) 2 – *x*, 1 – *y*, 1 – *z*; (d) 1½ – *x*, ½ + *y*, ½ – *z*; (e) 1 – *x*, -*y*, 1 – *z*; (f) 1 – *x*, 1 – *y*, 1 – *z*; (g) *x*, 1 + *y*, *z*.

1. Z. H. Zhou, Q. Xu, J. Lin and S. W. Ng, *Inorg. Chem. Commun*, 2007, **10**, 1461-1464.
2. J. Zhao and L. Xu, *Eur. J. Inorg. Chem*, 2011, **2011**, 4096-4102.
3. Z. H. Dang, J. Zhao and L. Xu, *Inorg. Chim. Acta.*, 2009, **362**, 2999-3004.
4. S. Duval, J. Marrot, C. Simonnet Jégat and E. Cadot, *Solid. State. Sci.*, 2009, **11**, 56-60.
5. S. Duval, F. Dumur, J. Marrot, C. Simonnet Jégat and E. Cadot, *Inorg. Chem. Commun.*, 2012, **18**, 11-14.
6. Z. H. Dang, S. Mou and L. Xu, *J. Solid. State. Chem.*, 2009, **182**, 2840-2845.
7. S. Duval, S. Floquet, C. Simonnet Jegat, J. Marrot, R. N. Biboum, B. Keita, L. Nadjo, M. Haouas, F. Taulelle and E. Cadot, *J. Am. Chem. Soc.*, 2010, **132**, 2069-2077.
8. J. F. Wu, D. M. Li, L. F. Cui, C. F. Zhuang, S. N. Song, T. G. Wang, J. Q. Xu, H. Q. Jia and N. H. Hu, *Appl. Organomet. Chem.*, 2007, **21**, 1033-1040.
9. W. B. Yan, Y. F. Deng, F. Z. Zhang, Z. H. Zhou, H. L. Wan and S. W. Ng, *Acta. Crystallogr. E.*, 2002, **58**, m22-m24.
10. D. Deb, S. Duley, S. Radenkovic, P. Bultinck, P. K. Chattaraj and M. Bhattacharjee, *Phys. Chem. Chem. Phys.*, 2012, **14**, 15579-15592.
11. B. M. Aas and P. Klüfers, *Eur. J. Inorg. Chem.*, 2017, **2017**, 2313-2320.
12. M. A. Walters, V. Vapnyar, A. Bolour, C. Incarvito and A. L. Rheingold, *Polyhedron*, 2003, **22**, 941-946.
13. W. Clegg, A. K. Powell and M. J. Ware, *Acta. Crystallogr. C.*, 1984, **C40**, 1822-1824.
14. T. Fujita, S. Ohba, Y. Nishida, A. Goto and T. Kokii, *Acta. Crystallogr. C.*, 1994, **C50**, 544-546.
15. G. C. Valle, G. G. Bombi, B. Corain, M. Favarato and P. Zatta, *Dalton Trans*, 1989, 1513-1517.
16. S. Abeysinghe, D. K. Unruh and T. Z. Forbes, *Inorg. Chem.*, 2013, **52**, 5991-5999.
17. H. G. Visser, *Acta. Crystallogr. E.*, 2006, **63**, m162-m164.
18. G. Novitchi, J. P. Costes, V. Ciornea, S. Shova, I. Filippova, Y. A. Simonov and A. Gulea, *Eur. J. Inorg. Chem.*, 2005, **2005**, 929-937.
19. V. Ciornea, L. Mingalieva, J. P. Costes, G. Novitchi, I. Filippova, R. T. Galeev, S. Shova, V. K. Voronkova and A. Gulea, *Inorg. Chim. Acta.*, 2008, **361**, 1947-1957.
20. L. V. Mingalieva, V. Ciornea, S. Shova, V. K. Voronkova, J. P. Costes, R. T. Galeev, A. Gulea and G. Novitchi, *Polyhedron*, 2012, **45**, 238-244.
21. G. Novitchi, V. Ciornea, S. Shova, A. Gulea, J. P. Costes and A. K. Powell, *Eur. J. Inorg. Chem.*, 2008, **2008**, 1778-1783.
22. G. Novitchi, V. Ciornea, J. P. Costes, A. Gulea, O. N. Kazheva, S. Shova and V. B. Arion, *Polyhedron*, 2010, **29**, 2258-2261.
23. M. Wolf and P. Klüfers, *Eur. J. Inorg. Chem.*, 2017, **2017**, 2303-2312.
24. W. Schmitt, P. A. Jordan, R. K. Henderson, G. R. Moore, C. E. Anson and A. K. Powell, *Coord. Chem. Rev.*, 2002, **228**, 115-126.
25. Y. G. Wei, S. W. Zhang and M. C. Shao, *Polyhedron*, 1997, **16**, 2307-2313.
26. J. Qian, J. Tian, W. Gu, S. Gao, L. Xin, S. Yan, J. Ribas, D. Liao and P. Cheng, *Dalton Trans*, 2008, DOI: 10.1039/b808916g, 6948-6952.