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Supporting Information

Oxalate bridged copper pyrazole complex templated Anderson-Evans cluster based solids

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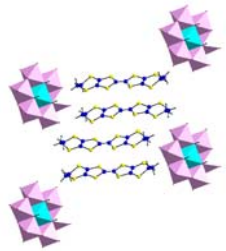
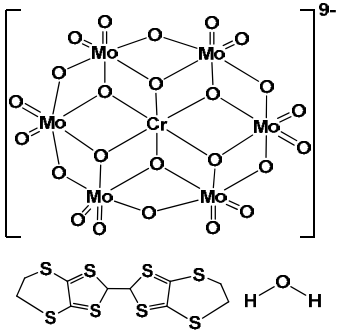
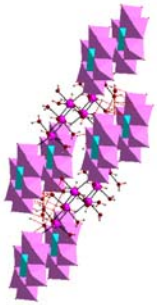
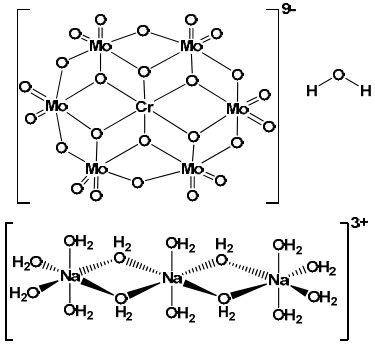
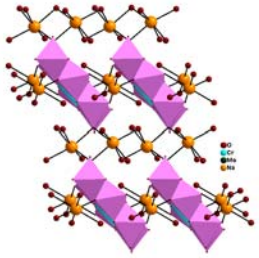
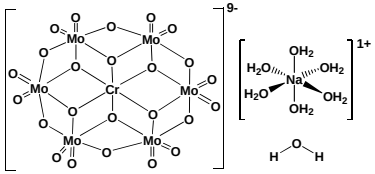
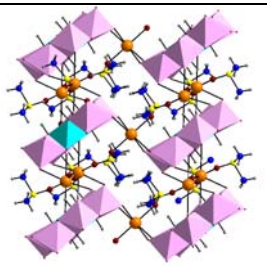
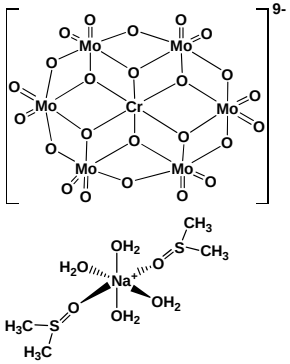
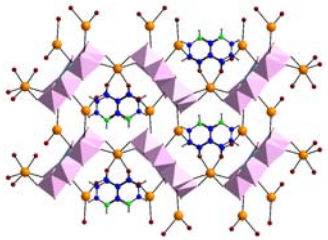
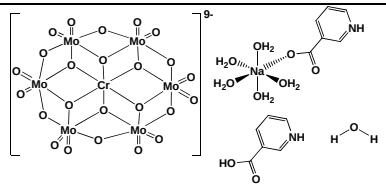
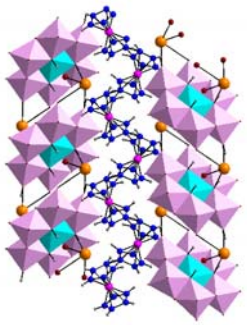
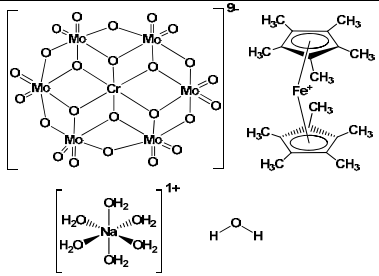
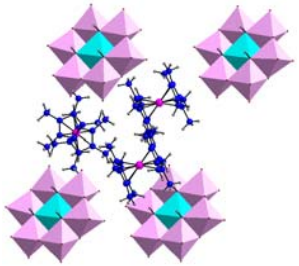
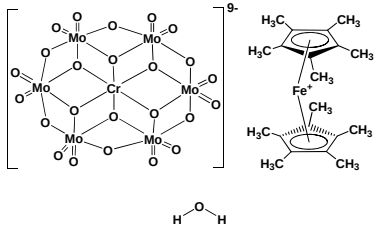
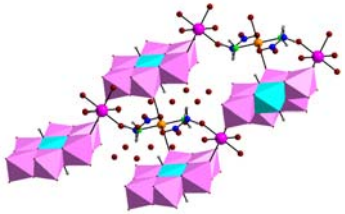
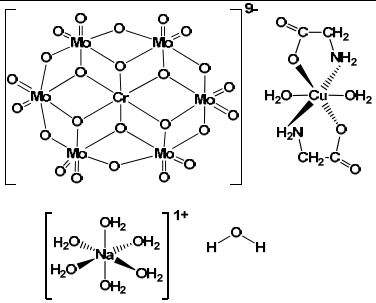
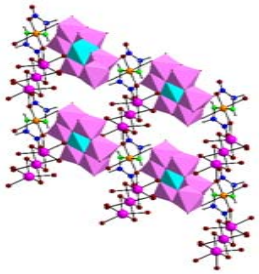
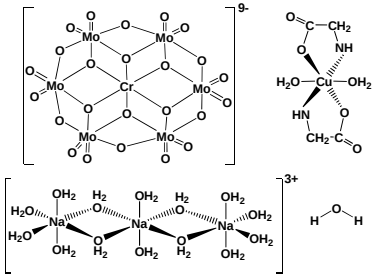
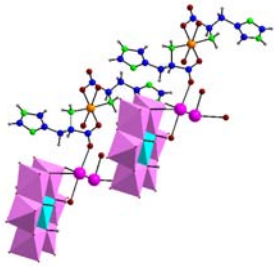
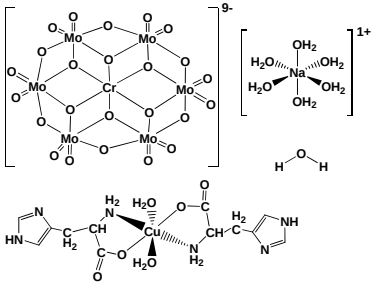
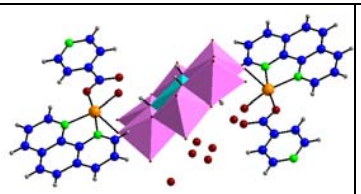
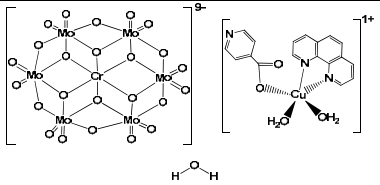
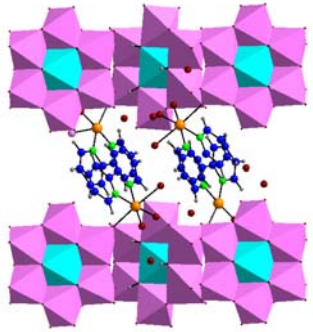
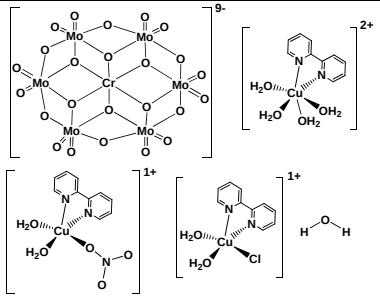
Table S1. Retrosynthetic analysis of Anderson-Evans type chromium molybdate cluster based solids reported in the literature along with tectons involved in each supramolecular reaction.

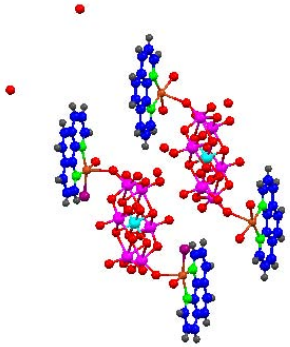
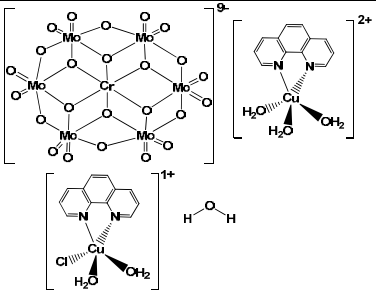
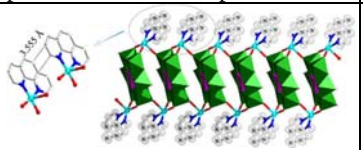
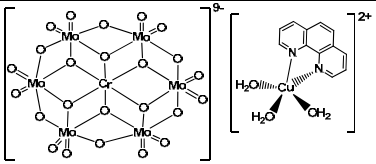
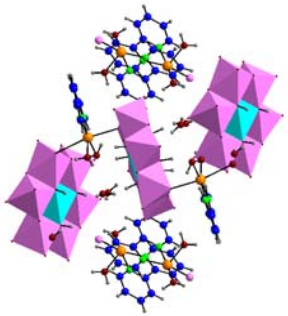
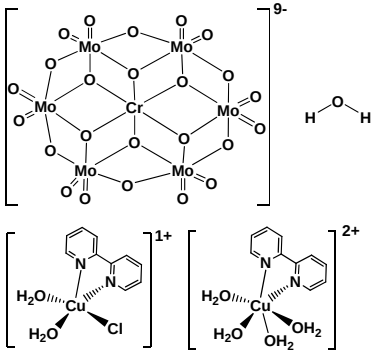
S.No.	Compound	Cell parameters	Experimental conditions	Structural description	Tectons	Reference
1.	(BEDT-TTF)$_4$[$H_6CrMo_6O_{24}$]·2H_2O [BEDT-TTF = bis(ethylenedithio) tetrathiafulvalene]	Triclinic *P*-1 *a* / Å = 5.9545(2) *b* / Å = 16.3767(6) *c* / Å = 21.8643(6) α /° = 110.829(2) β/° = 91.262(2) γ/° = 98.129(1) *V* / Å^3 = 1966.70(11) Z = 1	Galvanostatic oxidation using BEDT-TTF (10 mg), platinum wire electrodes and a constant current intensity of 1.2 mA. Solution of $Na_3[H_6CrMo_6O_{24}].nH_2O$ (A=Bu_4N^+ or Ph_4P^+)(100mg) in CH_2Cl_2 (20ml) was used as electrolyte.	 Both the cluster and the organic molecule are discrete ions.		*J. Cluster Sci.* **2003**, *14*, 193.

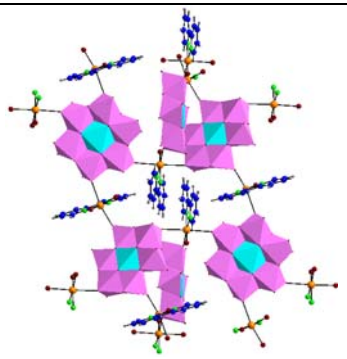
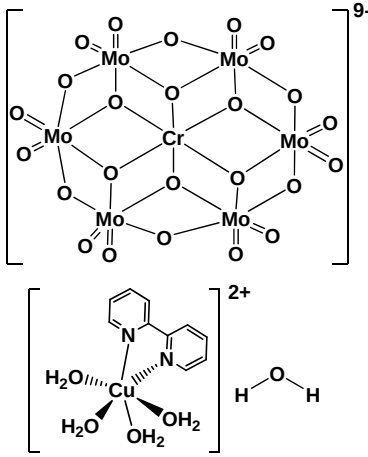
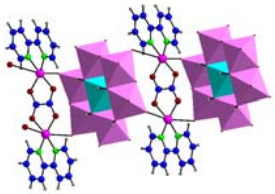
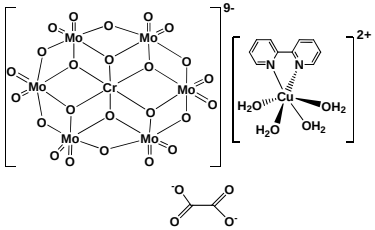
2.	$[\{Na_3(H_2O)_{11}\}\{H_6CrMo_6O_{24}\}].2H_2O$	Triclinic *P*-1 *a* / Å = 10.968 (2) *b* / Å = 11.686 (2) *c* / Å = 14.895 (3) α /° = 72.10 (3) β/° = 70.99 (3) γ/° = 66.90 (3) Z = 2	$Na_3[H_6CrMo_6O_{24}].nH_2O$ (3.8 g in 10 ml H_2O) to which a methanol-water (20 ml) solution in a volume ratio of 5:3 was added. The pH of the resulting solution was adjusted to 3.5 with acetic acid. The resulting solution was filtered and slowly evaporated at ambient temperature.	 The cluster is covalently linked to trimeric sodium hydrate into 1D chain.		*Acta Cryst. E.* **2006**, *62*, i190.
3.	$[Na_3\{H_6CrMo_6O_{24}\}].8H_2O$	Triclinic *P*-1 *a* / Å = 10.9080 (4) *b* / Å = 10.9807(4) *c* / Å = 6.4679 (2) α /° = 107.594(2) β/° = 84.438(2) γ/° =112.465(3) Z = 1	$Na_2MoO_4.2H_2O$ (145g in 300 ml H_2O)/ $Cr(NO_3)_3.9H_2O$(40g in 40 ml H_2O). pH was adjusted to **4.5** with concentrated HNO_3.	 The cluster is covalently linked by monomeric sodium hydrate and sodium hydrate chains into 3D framework.		*Inorg. Chem.* **1970**, *9*, 2228.
4.	$[Na_3\{H_6CrMo_6O_{24}\}].6DMSO$	Monoclinic *C*2/*c* *a* / Å = 25.37(2) *b* / Å = 14.632(2) *c* / Å = 15.455(6) β/° = 123.17(4) *V* /Å^3 = 4803(4) Z = 4	A vigorous stirring Of $Na_3[Cr(OH)_6Mo_6O_{18}].8H_2O$ in DMSO at 25-30 °C during several days.	 The cluster is covalently linked by sodium complex into 3D framework.		*Inorg. Chem.* **1998,** *37*, 1499.

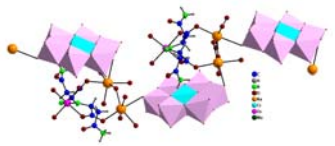
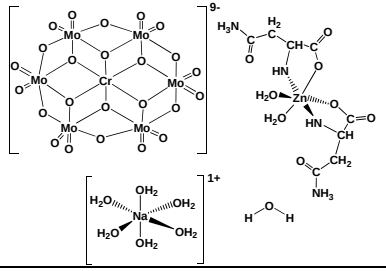
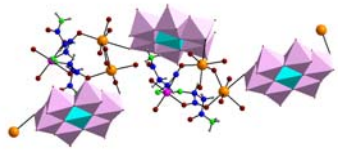
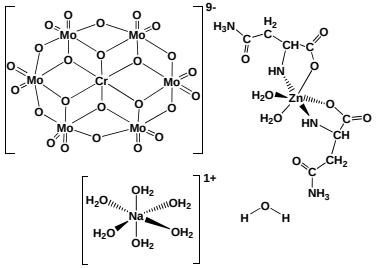
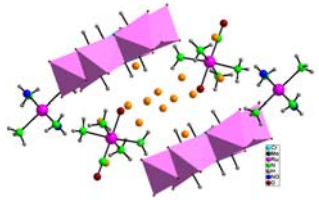
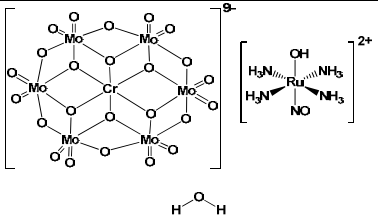
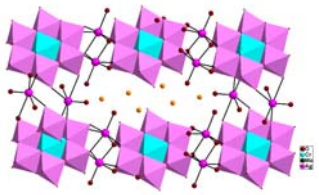
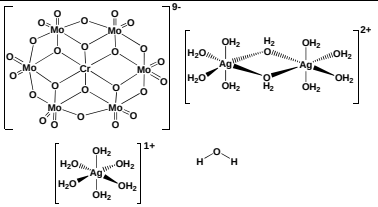
5.	$(C_6H_5NO_2)_2[\{Na_3(C_6H_5NO_2)_2\}\{H_6CrMo_6O_{24}\}]$ [$(C_6H_5NO_2)$ = pyridine-3-carboxylic acid]	Monoclinic *C*2/*c* *a* / Å = 22.045(4) *b* / Å = 9.4640(19) *c* / Å = 21.088(4) β/° = 98.56(3) *V* / Å^3 = 4350.9(15) Z = 4	Pyridine-3-carboxylic acid(2 mmol)/$NaClO_4.H_2O$ (1mmol)/$Na_3[CrMo_6H_6O_{24}].8H_2O$(1 mmol) in 50 ml H_2O at 80°C.	 The cluster is covalently linked by sodium and its complex into 2D sheet.		*J. Mol. Struct*. **2005**, *751*, 184.
6.	$\{Fe(C_5H_5)_2\}_2$ $[Na\{H_6CrMo_6O_{24}\}.3H_2O$ [C_5H_5 = cyclopentadienyl]	Monoclinic *P*21/*n* *a* / Å = 10.015(2) *b* / Å = 7.722(6) *c* / Å = 25.137(5) β/° = 90.626(9) *V* /Å^3 = 1944(2) Z = 2	Crystal growth was performed in a glass H-cell where the two compartments are separated by a fine porosity glass frit. $[Fe(C_5H_5)_2]BF_4$ (1mmol) is added to one compartment, and a concentrated solution of $Na_3[H_6CrMo_6O_{24}].8H_2O$ (0.33mmol) is added to the other one.	 The cluster is covalently linked by sodium hydrate into 1D chain and iron complex occurs as discrete.		*Inorg. Chem.* **1998,** *37*, 1499.
7.	$\{Fe(C_5Me_5)_2\}_3[H_6CrMo_6O_{24}].20H_2O$ [C_5Me_5 = pentamethyl cyclopentadienyl]	Triclinic *P*-1 *a* / Å = 12.489(3) *b* / Å = 14.113(3) *c* / Å = 15.662(4) α /° = 101.55(2) β/° = 105.82(2) γ/° = 110.23(2) *V* / Å^3 = 2355.7(9) Z = 1	$[Fe(C_5Me_5)_2]BF_4$(1mmol in 20mL)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$ (0.33mmol) in a small amount of 1/5 H_2O/CH_3CN.	 Both the cluster and the iron complex are discrete.		*Inorg. Chem.* **1998,** *37*, 1499.

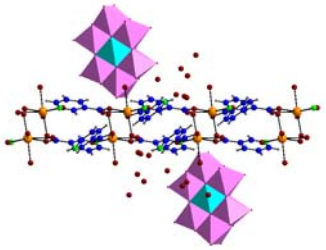
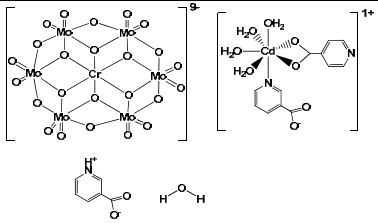
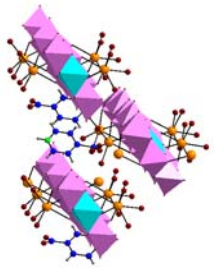
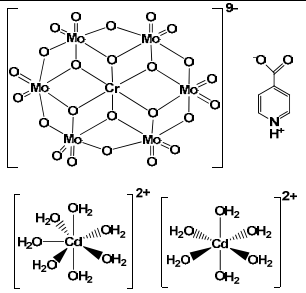
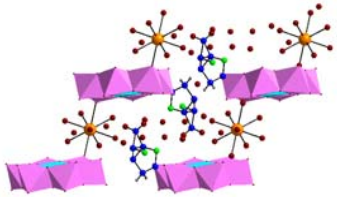
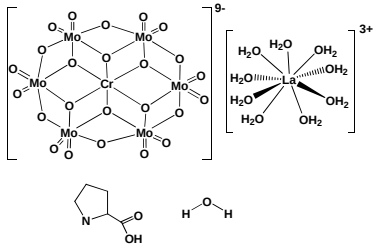
8.	[{Cu(Gly)$_2$}{Na(H$_2$O)$_4$(H$_6$CrMo$_6$O$_{24}$)}].9.5H$_2$O (Gly = glycine)	Triclinic *P*-1 *a* / Å = 10.684(2) *b* / Å = 10.960(2) *c* / Å = 10.979(2) α /° = 60.42(3) β/° = 63.10(3) γ/° = 78.87(3) *V* / Å^3 = 996.31(30) Z = 1	Na$_3$[H$_6$CrMo$_6$O$_{24}$].8H$_2$O (1.35 mmol)/ glycine (2.70 mmol)/ CuCl$_2$.2H$_2$O (1.35 mmol) in water (20 ml). The mixture was refluxed for 1 h at 80°C after the pH value of the solution was adjusted to 4.50 with diluted NaOH solution.	 1D chain formed between sodium hydrate and the cluster is bridged by copper complex.		*Inorg. Chem. Commun*. **2004**, *7*, 521.
9.	[Na$_3${Cu(Gly)$_2$}{H$_6$CrMo$_6$O$_{24}$}].13H$_2$O (Gly = Glycine)	Triclinic *P*-1 *a* / Å = 10.577(2) *b* / Å = 10.852(2) *c* / Å = 10.955(2) α /° = 60.31(3) β/° = 63.32(3) γ/° = 78.95(3) Z = 1	Glycine/Cu(CH$_3$COO)$_2$.H$_2$O/ NaClO$_4$.H$_2$O/ Na$_3$[H$_6$CrMo$_6$O$_{24}$].8H$_2$O. The mixture was refluxed for 2 h at 80°C. The filtrate was kept for 1 month at ambient conditions.	 1D chain formed between the cluster and copper complex is bridged by trimeric sodium hydrate.		*J. Cluster Sci*. **2008** *19*, 367.
10.	[{Cu(C$_6$H$_8$N$_3$O$_2$)(C$_6$H$_9$N$_3$O$_2$)(H$_2$O)$_2$}{Na(H$_2$O)}$_2${H$_6$CrMo$_6$O$_{24}$}].3H$_2$O (C$_6$H$_9$N$_3$O$_2$ = Histidine)	Triclinic *P*1 *a* / Å = 10.2053(16) *b* / Å = 11.2092(18) *c* / Å = 11.8049(19) α /° = 109.583(2) β/° = 95.353(2) γ/° = 109.081(2) *V* / Å^3 = 1170.8(3) Z = 1	CrCl$_3$.6H$_2$O (0.8 mmol)/ Na$_2$MoO$_4$.2H$_2$O (1.5 mmol)/Cu(CH$_3$COO)$_2$.2H$_2$O (0.5 mmol)/ Histidine (1 mmol) at room temperature. The final pH was adjusted to about 2.6 with conc. HCl. The filtrate was kept for 3 days.	 The cluster is covalently linked by sodium hydrate connected to copper complex.		*J. Mol. Struct*. **2009**, *931*, 50.

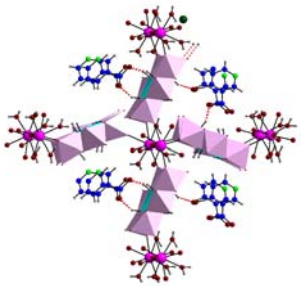
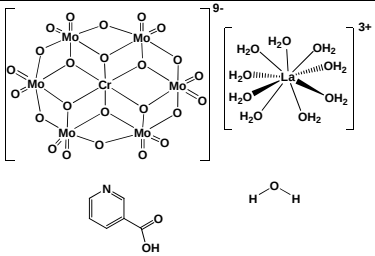
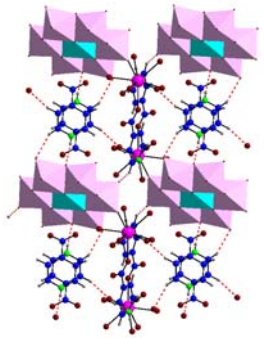
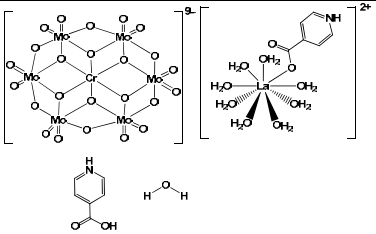
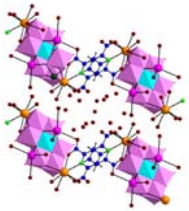
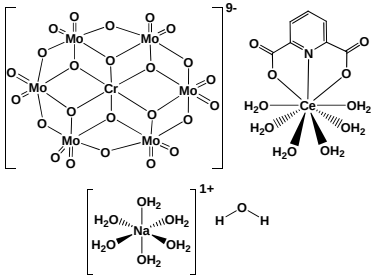
11.	[{Cu($C_6NO_2H_4$)(phen)(H_2O)}$_2$ {$H_6CrMo_6O_{24}$}](H_3O^+).5H_2O ($C_6NO_2H_4$ = pyridine-4-carboxylic acid)	Triclinic *P*-1 *a* / Å = 9.9418(9) *b* / Å = 9.9459(9) *c* / Å = 14.2493(12) α / ° = 81.4570(10) β/ ° = 83.0140(10) γ/ ° = 77.2240(10) *V* / Å^3 = 1353.1(2) Z = 1	pyridine-4-carboxylic acid (0.27 mmol)/ phen (0.60 mmol)/ Cu(NO_3)$_2$.3H_2O (0.60 mmol) in H_2O-methanol. Na_2MoO_4.2H_2O (3.72mmol)/ Cr(NO_3)$_3$.6H_2O (1.50 mmol) in H_2O. The final pH of the solution was adjusted to 2.6 with the dilute HNO_3 solution (3 M). The filtrate was kept at room temperature.	 The cluster is derivatized by copper complex.		*J. Mol. Struct.* **2009**, *920*, 284.
12.	[{Cu(2,2'-bpy)(H_2O)$_3$}$_2$ {$H_6CrMo_6O_{24}$}] [{Cu(2,2'-bpy) (H_2O)Cl}{Cu(2,2'-bpy)(H_2O)(NO_3)} {$H_6CrMo_6O_{24}$}].18H_2O (2,2'-bpy = 2,2'-bipyridine)	Triclinic *P*-1 *a* / Å = 13.252(3) *b* / Å = 13.791(3) *c* / Å = 14.277(3) α /° = 90.71(3) β/° = 108.34(3) γ/° = 90.40(3) *V* / Å^3 = 2476.3(9) Z = 1	Na_2MoO_4.2H_2O (3.72mmol) in 30mL of water and the pH of the solution was adjusted with the dilute HNO_3(3M) to approx. 4.5, then a solution of $CrCl_3$.6H_2O (1.12mmol) in water (10mL) was added. $CuCl_2$.2H_2O (0.80mmol)/ 2,2'-bipyridine(0.80 mmol) in H_2O - methanol solution, and then it was added to the upper solution with stirring. The pH of the final solution was adjusted to 2.6 with the dilute HNO_3 (3M). The filtrate was kept for five days at ambient conditions.	 The cluster is derivatized by copper bipyridyl complex.		*J. Solid State Chem.* **2009**, *182*, 49.

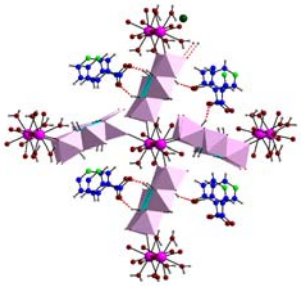
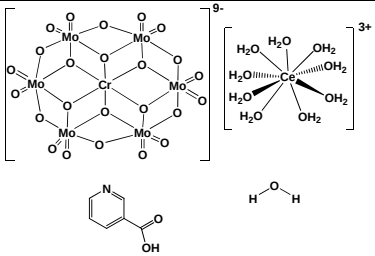
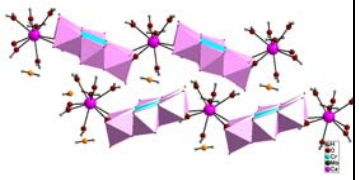
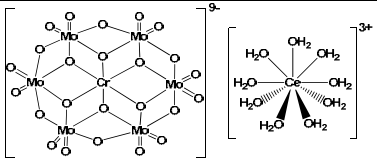
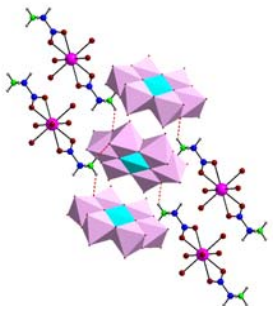
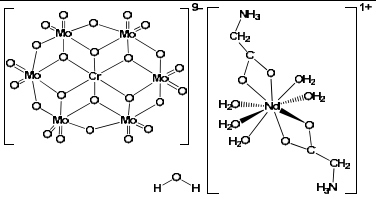
13.	[{(Cu(phen)(H_2O)$_2$)$_2$($H_6CrMo_6O_{24}$)}{ (Cu(phen)(H_2O)Cl($H_6CrMo_6O_{24}$))$_2$}]. 5H_2O [phen = 1,10-phenanthroline]	Triclinic *P*-1 *a* / Å = 10.8867(5) *b* / Å = 15.2504(7) *c* / Å = 15.7022(7) α /° = 64.9850(10) β/° = 83.0430(10) γ/° = 71.1570(10) *V* / Å^3 = 2235.47(18) Z = 1	$CrCl_3.6H_2O$ (3.75 mmol)/ $Na_2MoO_4.2H_2O$ (14.46 mmol)/10 ml acetic acid/ 1,10-Phenanthroline (1mmol) /$Cu(NO_3)_2.3H_2O$ (2.9 mmol) in 200 ml H_2O at 90°C. pH was adjusted to 2.6 with conc.HCl.	 The cluster is derivatized by two different copper phenanthroline complex.		*Inorg. Chem.* **2005**, *44*, 8846.
14.	[{Cu(phen)}$_2${$H_5CrMo_6O_{24}$}] (phen = 1,10-phenanthroline)	Monoclinic *P*2(1)/*n* *a* / Å = 5.66710(10) *b* / Å = 21.3723(5) *c* / Å = 14.7092(3) β/° = 98.10(10) *V* / Å^3 = 1763.79(6) Z = 2	$Na_2MoO_4.2H_2O$ (1.86 mmol)/ $CuCl_2.2H_2O$(0.3 mmol)/ $CrCl_3.6H_2O$(0.75 mmol)/ phen(0.2 mmol)/ H_2O(10 mL) at 165 °C for 120 h. The solution was slowly cooled to room-temperature at a rate of 10 °Ch^{-1}.	 The cluster is covalently linked by copper phenanthroline complex into 1D chain.		*J. Mol. Struct.* **2010**, *967*, 15.
15.	[Cu(2,2'-bpy)(H_2O)$_2$Cl][{Cu(2,2'-bpy)(H_2O)$_2$}{$H_6CrMo_6O_{24}$}]. 4H_2O (2,2'-bpy = 2,2'-bipyridine)	Triclinic *P*-1 *a* / Å = 11.244(2) *b* / Å = 14.566(3) *c* / Å = 15.330(3) α /° = 112.21(3) β/° = 106.65(3) γ/° = 93.90(3) *V* / Å^3 = 2182.6(8) Z = 2	$Na_2MoO_4.2H_2O$ (3.72mmol) in 30mL of water and the pH of the solution was adjusted with the dilute HCl(3M) to approx. 4.5, then a solution of $CrCl_3.6H_2O$(1.12mmol) in water (10mL) was added. $CuCl_2.2H_2O$ (0.80mmol)/ 2,2'-bipyridine(0.80 mmol) in H_2O - methanol solution, and then it was added to the upper solution with stirring. The pH of the	 The cluster is covalently linked by one type of copper bipyridyl complex into 1D chains. A		*J. Solid State Chem.* **2009**, *182*, 49.

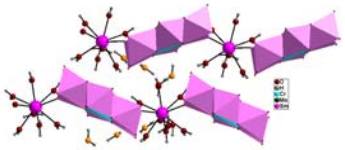
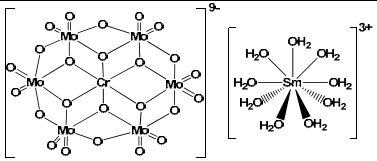
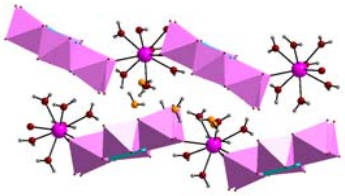
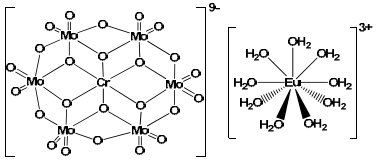
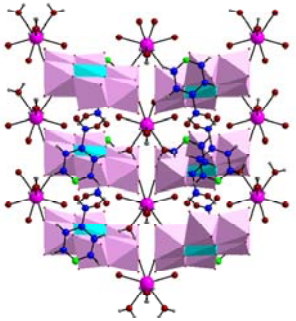
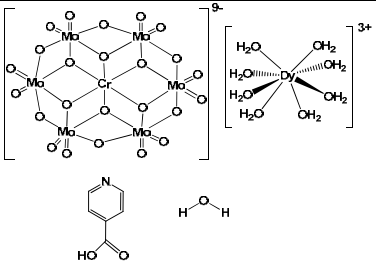
			final solution was adjusted to 2.6 with the dilute HCl (3M). The filtrate was kept for five days at ambient conditions.	different copper bipyridyl complex occurs as discrete cation.		
16.	$(H_3O)[\{Cu(2,2'\text{-bpy})(H_2O)_2\}_2\{Cu(2,2'\text{-bpy})(H_2O)\}_2\{H_6CrMo_6O_{24}\}]_3.36H_2O$ (2,2'-bpy = 2,2'-bipyridine)	Triclinic *P*-1 *a* / Å = 14.1896(13) *b* / Å = 15.6768(14) *c* / Å = 16.2269(15) α /° = 65.4780(10) β/° = 70.5120(10) γ/° = 80.5860(10) *V* / Å^3 = 3094.6(5) Z = 1	$Na_2MoO_4.2H_2O$ (3.72mmol) in 30mL of water and the pH of the solution was adjusted with the dilute HNO_3(3M) to approx. 4.5, then a solution of $Cr(NO_3)_3.9H_2O$ (1.12mmol) in water (10mL) was added. $Cu(NO_3)_2.3H_2O$(0.8mmol) /2,2'-bipyridine(0.8mmol) in H_2O - methanol solution, and then it was added to the upper solution with stirring. The pH of the final solution was adjusted to 2.6 with the dilute HNO_3 (3M). The filtrate was kept for five days at ambient conditions.	 The cluster is covalently linked by copper bipyridyl complex into 2D sheet.		*J. Solid State Chem.* **2009**, *182*, 49.
17.	$[\{Cu_2(bpy)_2(\mu\text{-}ox)\}\{H_7CrMo_6O_{24}\}]$ (bpy = 2,2'-bipyridine) (ox = oxalic acid)	Orthorhombic *Pna*2 *a* / Å = 14.2385(7) *b* / Å = 26.3312(13) *c* / Å = 10.2825(5) *V* / Å^3 = 3855.1(3) Z = 4	$CuCl_2.2H_2O$(0.6mmol)/ 2,2'-bpy(0.6mmol)/ oxalic acid(0.3mmol) in 10 ml H_2O and 10ml methanol/ $Na_2MoO_4.2H_2O$ (3.72mmol)/ $CrCl_3.6H_2O$(1.12mmol) in 30ml H_2O/3M dil HCl.	 The cluster is covalently linked by dinuclear copper bipyridyl complex bridged by oxalate units forming 1D chain.		*Inorg. Chem.* **2007**, *46*, 3541.

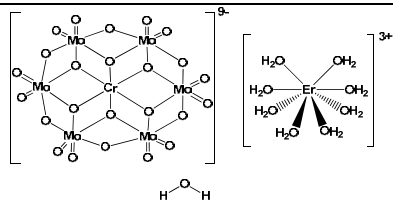
18.	$(C_4NH_7O_4)[\{(Zn(L\text{-}C_4H_8N_2O_3)_2)(Na_2(H_2O)_9)\}_2\{H_6CrMo_6O_{24}\}_2].7H_2O$ [(L- $C_4H_8N_2O_3$) = L-asparagine]	Orthorhombic $P\,2_12_12$ a / Å = 20.405(4) b / Å = 21.821(4) c / Å = 10.917(2) V / Å^3 = 4860.88(17) Z = 4	L-asparagine (2 mmol)/ $Zn(OAc)_2.H_2O$ (1 mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$ (0.5 mmol) in 50ml H_2O at 80°C. pH was adjusted to 4.0.	 The cluster is covalently linked by zinc complex in 1D chain.		*Inorg. Chem. Commun*. **2008**, *11*, 914.
19.	$(C_4NH_7O_4)[\{(Zn(D\text{-}C_4H_8N_2O_3)_2)(Na_2(H_2O)_9)\}_2\{H_6CrMo_6O_{24}\}_2].7H_2O$ [(D- $C_4H_8N_2O_3$) = D-asparagine]	Orthorhombic $P\,2_12_12$ a / Å = 20.454(4) b / Å = 21.822(4) c / Å = 10.918(2) V / Å^3 = 4873.22(17) Z = 4	D-asparagine (2 mmol)/ $Zn(OAc)_2.H_2O$ (1 mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$ (0.5 mmol) in 50ml H_2O at 80°C. pH was adjusted to 4.0.	 The cluster is covalently linked by zinc complex in 1D chain.		*Inorg. Chem. Commun*. **2008**, *11*, 914.
20.	$\{RuNO(NH_3)_4OH\}_3[\{H_6CrMo_6O_{24}\}_2].15H_2O$	Triclinic P-1 a / Å = 10.5858(2) b / Å = 11.0407(2) c / Å = 16.8077(4) α /° = 76.919(1) β/° = 73.774(1) γ/° = 84.090(1) V / Å^3 = 1835.55(6) Z = 1	Diffusing 10 ml $Na_3[H_6CrMo_6O_{24}].8H_2O$ (0.3 mmol) and 5 ml $[RuNO(NH_3)_4OH]Cl_2$(0.45 mmol) in H_2O for a month.	 Both the cluster and ruthenium complex are discrete.		*J. Cluster Sci*. **2006**, *17*, 303.
21.	$[\{Ag_3(H_2O)_4\}\{H_6CrMo_6O_{24}\}].3H_2O$	Triclinic P-1 a / Å = 6.2052(12) b / Å = 14.185(3) c / Å = 15.077(3) α /° = 90.68(3) β/° = 90.08(3) γ/° = 93.82(3) V / Å^3 = 1324.0(5) Z = 2	$AgNO_3$(1 mmol)/aspartic acid (1 mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$(1 mmol) in 40 ml H_2O at 80 °C. Diffraction-quality crystals were obtained by recrystallization from 20 ml of hot water.	 The cluster is covalently linked into a 3D framework by silver hydrate.		*Cryst. Growth Des.* **2006**, *6*, 1107.

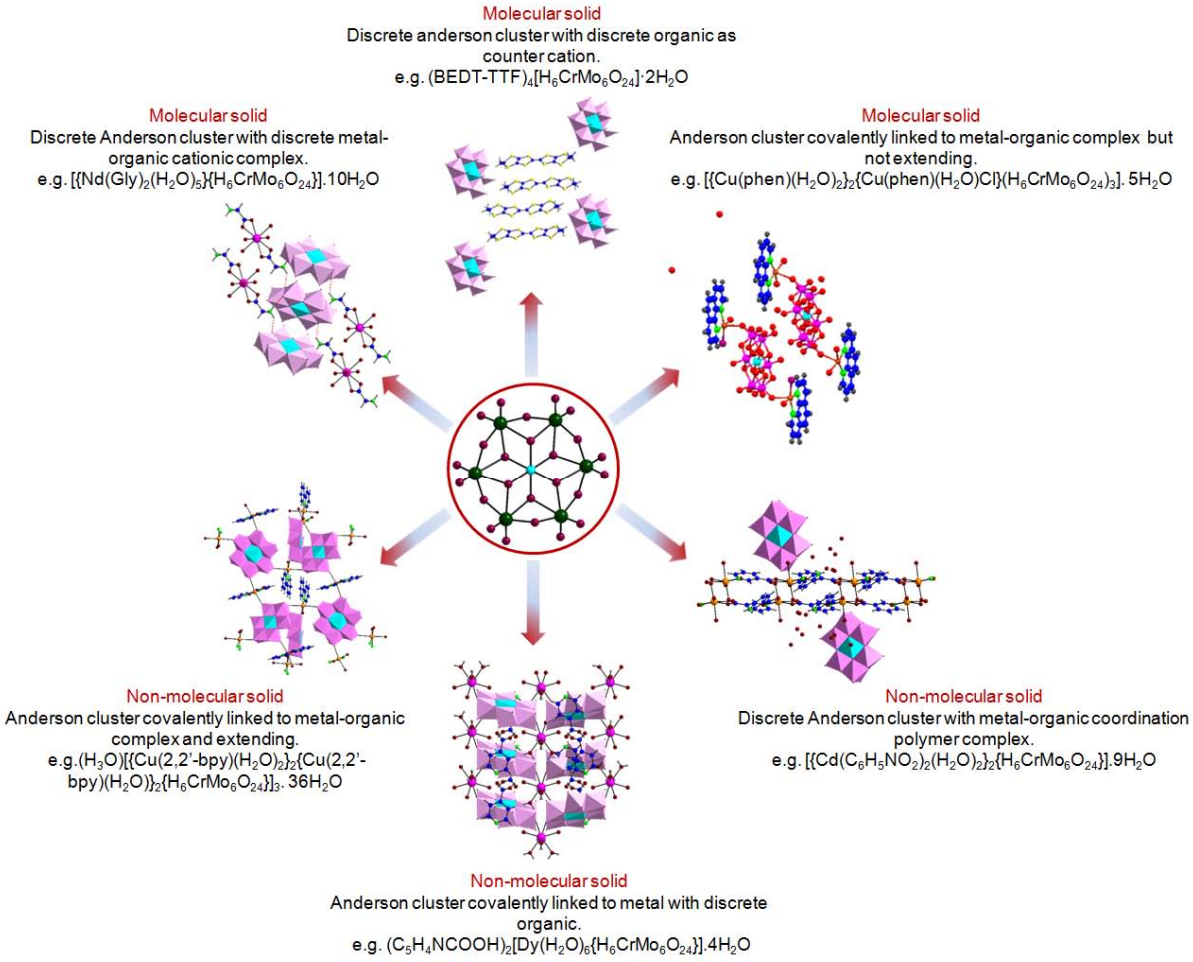
22.	$[\{(H_2O)_2(HC_6H_4NO_2)Cd(C_6H_5NO_2)\}_2\{H_6CrMo_6O_{24}\}].9H_2O$ ($C_6H_5NO_2$ = pyridine-3-carboxylic acid)	Triclinic *P*-1 *a* / Å = 7.9922(16) *b* / Å = 13.861(3) *c* / Å = 14.357(3) α /° = 74.63(3) β/° = 84.59(3) γ/° = 82.96(3) *V* / Å^3 = 1518.8(5) Z = 1	Pyridine-3-carboxylic acid (1 mmol)/ $Cd(NO_3)_2.2H_2O$(1 mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$(0.5 mmol) were refluxed for 2 h at 80°C, and then filtered. The filtrate was kept for 4 weeks under ambient conditions.	 The cluster occurs as discrete anion for the cationic 1D coordination polymeric chain made of cadmium pyridine-3-carboxylate.		*J. Mol. Struct.* **2009**, *933*, 86.
23.	$[\{Cd_3(H_2O)_{14}\}\{H_6CrMo_6O_{24}\}_2](C_6H_5NO_2)_4$ ($C_6H_5NO_2$ = pyridine-4-carboxylic acid)	Monoclinic *Pc* *a* / Å = 12.639(3) *b* / Å = 10.761(2) *c* / Å = 13.777(3) β/° = 104.29(3) *V* / Å^3 = 1815.8(6) Z = 1	Pyridine-4-carboxylic acid (1 mmol)/ $Cd(NO_3)_2.2H_2O$ (1 mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$ (0.5 mmol) were refluxed for 2 h at 80°C, and then filtered. The filtrate was kept for 3 weeks under ambient conditions.	 The cluster is covalently linked by cadmium hydrate into 1D chain with organic as counter cation.		*J. Mol. Struct.* **2009**, *933*, 86.
24.	$(C_5H_9NO_2)_2[La(H_2O)_7\{H_6CrMo_6O_{24}\}].11H_2O$ ($C_5H_9NO_2$ = Proline)	Monoclinic *C*2/*c* *a* / Å = 26.257(5) *b* / Å = 11.526(2) *c* / Å = 19.890(4) β/° = 127.44(3) *V* /Å^3 = 4779.4(17) Z = 4	Proline (1.40 mmol)/ $La(NO_3)_3.7H_2O$(1.40 mmol)/ $Na_3(H_6CrMo_6O_{24}).8H_2O$ (1.35 mmol) at 80°C for 1 h. The filtrate was kept for two weeks at ambient conditions.	 The cluster is covalently linked by lanthanum hydrate in 2D sheet.		*Inorg. Chem. Commun.* **2004**, *7*, 356.

25.	$(C_6NO_2H_5)_2[La(H_2O)_5\{H_6CrMo_6O_{24}\}]$**.** $0.5H_2O$ [$(C_6NO_2H_5)$ = pyridine-3-carboxylic acid]	Orthorhombic *Pmn*21 *a* / Å = 15.080(3) *b* / Å = 11.630(2) *c* / Å = 23.096(5) *V* / $Å^3$ = 4050.6(14) Z = 4	Pyridine-3-carboxylic acid(0.5 mmol)/ $La(NO_3)_3.6H_2O$(0.5 mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$(0.5 mmol) in 20 ml H_2O at 80 °C.	 The cluster is covalently linked by lanthanum hydrate in 2D sheets.		*Eur. J. Inorg. Chem.* **2005**, 854.
26.	$(C_6H_5NO_2)[\{La(C_6H_5NO_2)(H_2O)_7\}\{H_6CrMo_6O_{24}\}].10.5H_2O$ [$(C_6H_5NO_2)$ = Pyridine-4-carboxylic acid]	Triclinic *P*-1 *a* / Å = 11.071(2) *b* / Å = 13.252(3) *c* / Å = 17.318(4) α /° = 91.73(3) β/° = 93.94(3) γ/° = 94.46(3) *V* / $Å^3$ = 2525.5(9) Z = 2	Pyridine-4-carboxylic acid(2mmol)/$LaCl_3.7H_2O$(1mmol)/$Na_3[H_6CrMo_6O_{24}]$. $8H_2O$(1 mmol) in 30 ml H_2O at 80°C.	 Both the cluster and lanthanum complex are discrete.		*J. Mol. Struct.* **2005**, *743*, 117.
27.	$Na[\{Ce(dipic)(H_2O)_3\}_2\{H_6CrMo_6O_{24}\}].13H_2O$ (H_2dipic = pyridine-2,6-dicarboxylic acid)	Triclinic *P*-1 *a* / Å = 9.2152(18) *b* / Å = 12.140(2) *c* / Å = 13.707(3) α /° = 70.99(3) β/° = 75.04(3) γ/° = 72.22(3) *V* / $Å^3$ = 1359.0(5) Z = 1	H_2dipic (1 mmol)/ $Ce(NO_3)_3.6H_2O$ (1 mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$ (1 mmol) in 60 ml of water at 50°C for 1 h. The filtrate was kept for one month under ambient conditions.	 The cluster is covalently linked through cerium hydrate and sodium hydrate complexes.		*Trans. Metal Chem.* **2006**, *31*, 770.

28.	$(C_6NO_2H_5)_2[Ce(H_2O)_5\{H_6CrMo_6O_{24}\}]$**.** $0.5H_2O$ [$C_6NO_2H_5$ = pyridine-3-carboxylic acid]	Orthorhombic *Pmn*21 *a* / Å = 15.0314(9) *b* / Å = 11.6090(7) *c* / Å = 23.0481(14) *V* / $Å^3$ = 4021.9(4) Z = 4	Pyridine-3-carboxylic acid(0.5 mmol)/ $Ce(NO_3)_3$**.**$6H_2O$(0.5 mmol)/ $Na_3[H_6CrMo_6O_{24}]$**.**$8H_2O$(0.5 mmol) in 20 ml H_2O at 80 °C.	 The cluster is covalently linked by cerium hydrate into 2D sheets and organic molecule occur as counter cation.		*Eur. J. Inorg. Chem.* **2005**, 854.
29.	$[Ce(H_2O)_7\{H_6CrMo_6O_{24}\}]$. $4H_2O$	Orthorhombic *Pca*2 *a* /Å = 11.8614(3) *b* / Å = 11.0038 (3) *c* / Å = 22.6117 (6) *V* / $Å^3$ = 2951.29(13) Z = 4	$Na_3[H_6CrMo_6O_{24}]$.$8H_2O$ (0.1mmol)/$Ce(NO_3)_3{\cdot}6H_2O$ (0.2mmol) in 25ml H_2O at 60°C.	 The cluster is covalently linked by cerium hydrate into 1D chains.		*Z. Anorg. Allg. Chem.* **2008**, 758.
30.	$[\{Nd(C_2H_5NO_2)_2(H_2O)_5\}\{H_6CrMo_6O_{24}\}].10H_2O$ [$(C_2H_5NO_2)$ = Glycine]	Monoclinic *C*2/*c* *a* / Å = 33.202(7) *b* / Å = 10.733(2) *c* / Å = 11.910(2) β/° = 106.38(3) *V* / $Å^3$ = 4071.9(14) Z = 4	Glycine(2mmol)/$Nd(ClO_4)_3$(1mmol)/$Na_3[H_6CrMo_6O_{24}]$. $8H_2O$(1 mmol) at room temperature.	 Both the cluster and neodymium complex are discrete.		*J. Mol. Struct.* **2005**, *743*, 117.

31.	$[Sm(H_2O)_7\{H_6CrMo_6O_{24}\}].4H_2O$	Orthorhombic *Pca*2 *a* / Å = 11.8289(4) *b* / Å = 10.9649(4) *c* / Å = 22.4370(7) *V* / Å^3 = 2910.14(17) Z = 4	$Na_3[H_6CrMo_6O_{24}].8H_2O$(0.1mmol)/ $Sm(NO_3)_3{\cdot}6H_2O$ (0.2mmol) in 25ml H_2O at 60°C.	 The cluster is covalently linked by samarium hydrate into 1D chains.		*Z. Anorg. Allg. Chem.* **2008**, 758.
32.	$[Eu(H_2O)_7\{H_6CrMo_6O_{24}\}]{\cdot}4H_2O$	Orthorhombic *Pca*2 *a* / Å = 11.832(5) *b* / Å = 10.966(5) *c* / Å = 22.425(5) *V* / Å^3 = 2909.6(19) Z = 4	$Na_3[H_6CrMo_6O_{24}].8H_2O$(0.1mmol)/ $Eu(NO_3)_3{\cdot}6H_2O$ (0.2mmol) in 25ml H_2O at 60°C.	 The cluster is covalently linked by europium hydrate into 1D chains.		*Z. Anorg. Allg. Chem.* **2008**, 758.
33.	$(C_6H_5NO_2)_2[Dy(H_2O)_6\{H_6CrMo_6O_{24}\}].4H_2O$ [$(C_6H_5NO_2)$ = pyridine-4-carboxylic acid]	Monoclinic *C*2/*c* *a* / Å = 18.276(4) *b* / Å = 12.549(3) *c* / Å = 17.822(4) β/° = 103.90(3) *V* /Å^3 = 3967.7(14) Z = 4	Pyridine-4-carboxylic acid(2 mmol)/$Dy(ClO_4)_3$(1 mmol)/$Na_3[H_6CrMo_6O_{24}].8H_2O$(1 mmol) in 50 ml H_2O.	 The cluster is covalently linked by dysprosium hydrate in 2D sheet.		*J. Mol. Struct.* **2005**, *751*, 184.

34.	$[\{Er_2(H_2O)_{14}(H_6CrMo_6O_{24})\}\{H_6CrMo_6O_{24}\}].14H_2O$	Triclinic *P*-1 *a* / Å = 11.046 (5) *b* / Å = 11.653 (5) *c* / Å = 13.935 (5) α /° = 75.006 (5) β/° = 84.497(5) γ/° = 89.515(5) *V* / $Å^3$ = 1724.4(12) Z = 1	Hexanedioic(0.5mmol)/ $Er(NO_3)_3.6H_2O$(0.2mmol)/ $Na_3[H_6CrMo_6O_{24}].8H_2O$ (0.1mmol) in 25 ml H_2O at 60°C.	 The cluster is discrete as well as derivatized with erbium hydrate.		*J. Chem. Crystallogr*. **2008**, *38*, 695.



Scheme S1. Classification of Anderson-Evans cluster based solids.

Table S2. Bond distances for the water – water interactions in **1** and **3** – **5**.

1	Bond distance (Å)	**3**	Bond distance (Å)
O1w --- O8w	2.710	O1w --- O2w	2.492
O7w --- O8w	2.799	O2w --- O4w	3.062
O6w --- O8w	3.071	O3w --- O4w	2.855
O6w --- O10w	2.879	O3w --- O5w	3.243
O4w --- O10w	3.047	O4w --- O5w	3.173
O4w --- O9w	2.746	**4**	
O5w --- O9w	3.075	O1w --- O2w	2.885
O5w --- O7w	2.865	O2w --- O3w	3.359
O9w --- O11w	2.761	O3w --- O4w	3.409
O3w --- O5w	3.200	O1w --- O3w	3.171
O3w --- O9w	3.090	O1w --- O4w	3.173
O2w --- O3w	2.779	O4w --- O4w	2.726
O2w --- O11w	2.722	**5**	
O11w --- O12w	2.604	O1w --- O2w	3.079
		O2w --- O4w	3.146
		O3w --- O4w	3.092
		O1w --- O4w	3.127
		O1w --- O4w	3.587
		O3w --- O3w	1.722

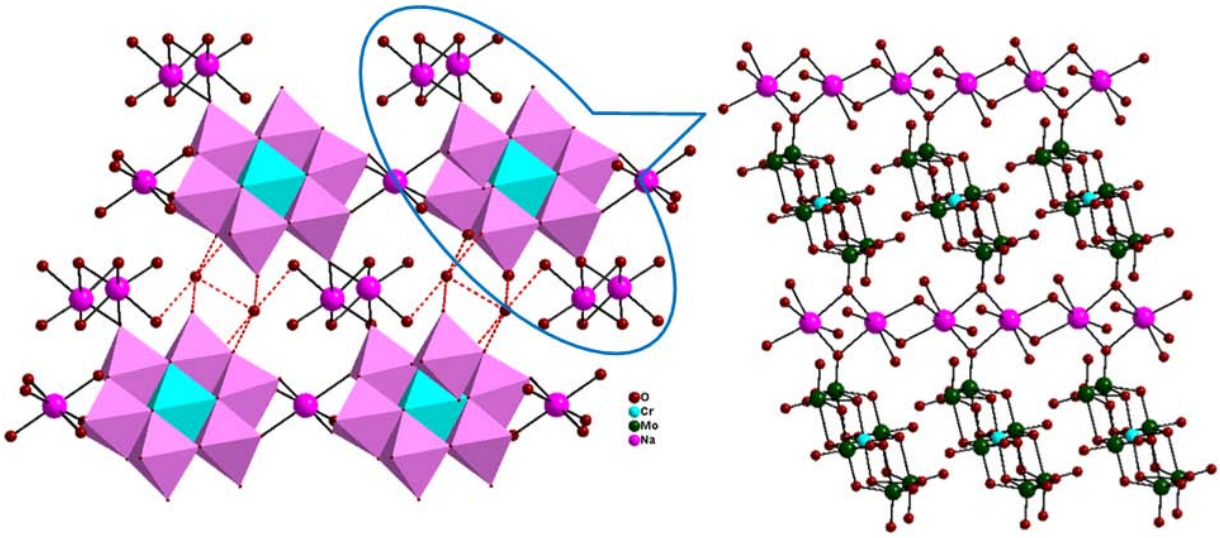


Fig. S1. Three-dimensional framework in **2**. A chain of sodium octahedra bridge Anderson cluster forming 2D sheets in **2**.

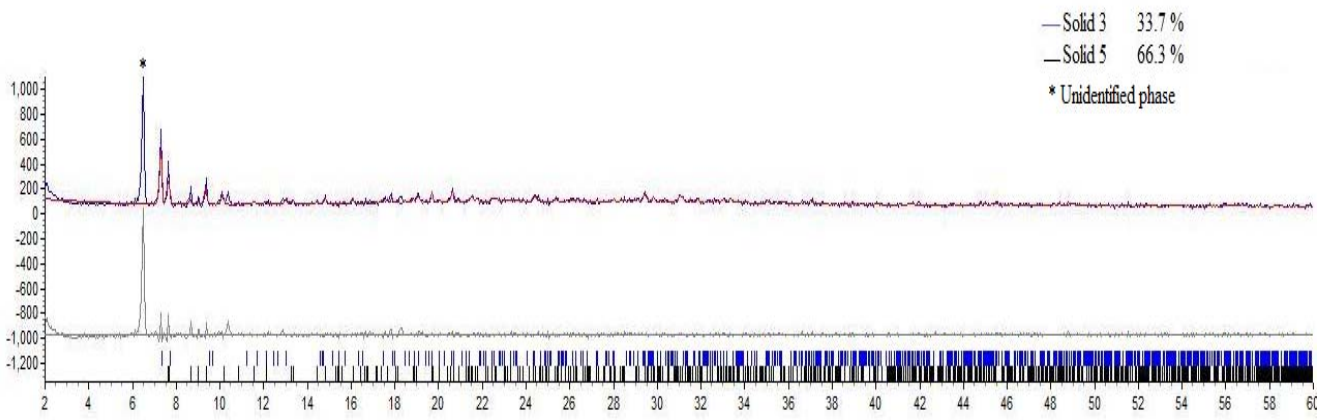


Fig. S2. Rietveld refinement plot of blue powder obtained in the absence of methanol matched with **3** and **5.** Rwp = 7.23, Rp = 6.41. * corresponds to an unidentified phase.

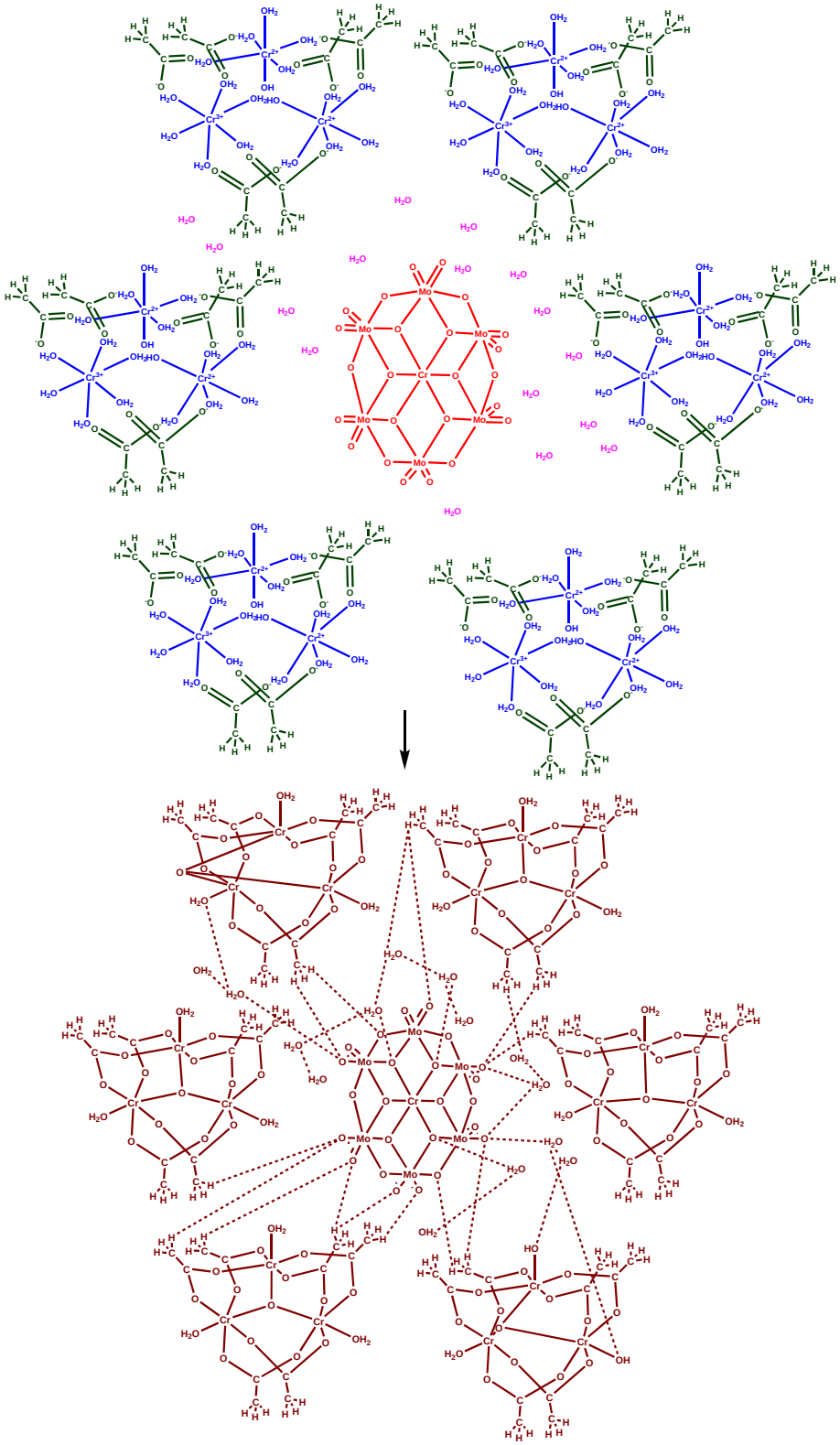


Fig. S3. Crystallization of [{$Cr_3(O)(CH_3COO)_6(H_2O)_3$}$_2${$H_3CrMo_6O_{24}$}].24$H_2O$, **1** from the supramolecular aggregation of three tectons: the two ionic clusters Anderson-Evans and trinuclear chromium along with mediating H_2O molecules; charge compensation is accounted for by protonation of the Anderson cluster.

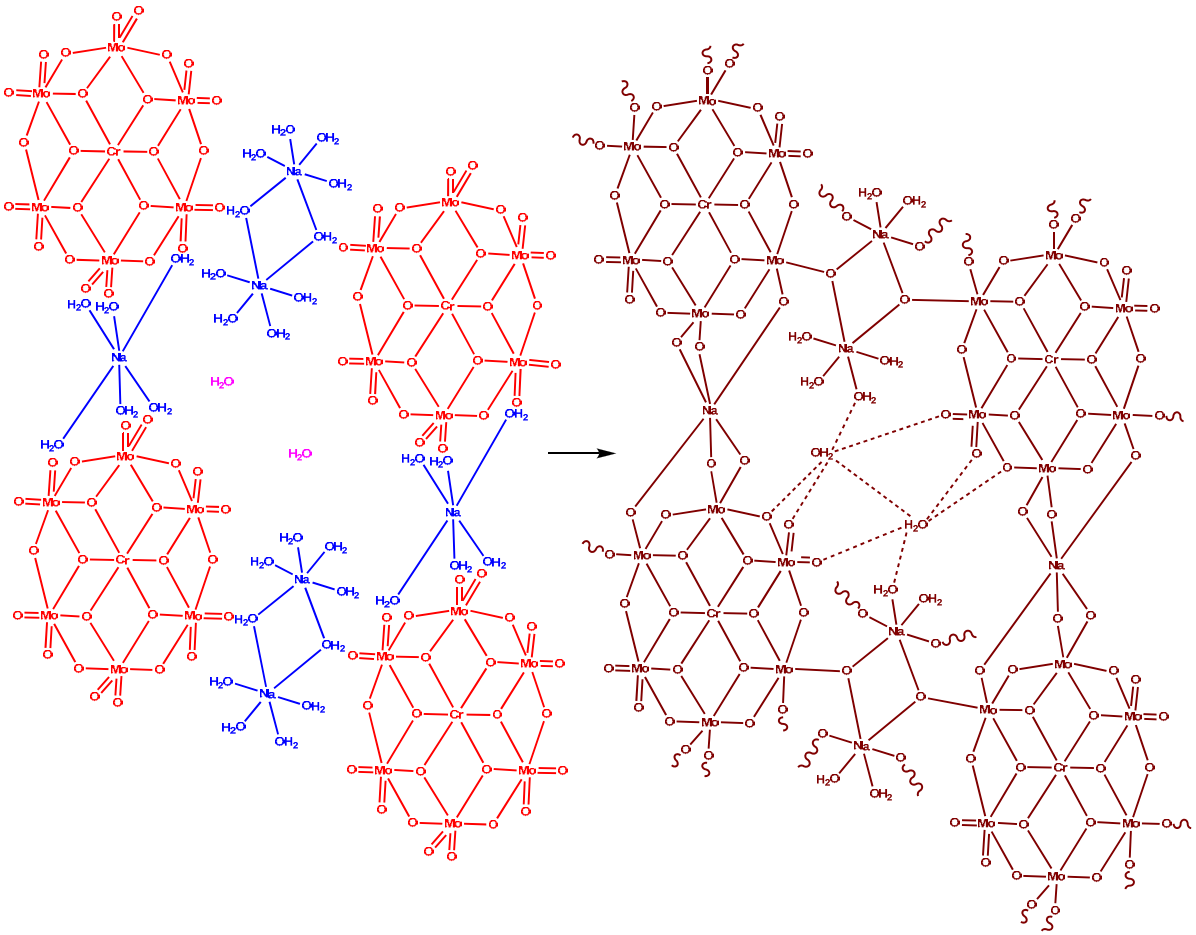


Fig. S4. Crystallization of $[\{Na\{Na(H_2O)_3\}_2\{H_6CrMo_6O_{24}\}].2H_2O$, **2** is an engineering of the four tectons $\{H_nCrMo_6O_{24}\}$, dimeric $\{Na_2(H_2O)_{10}\}^{2+}$, monomeric $\{Na(H_2O)_6\}^{1+}$ and H_2O at the molecular level. While monomeric sodium condenses with Anderson cluster in a tridentate mode to form 1D chains, dimeric sodium hydrates aggregate in an extended manner simultaneously bridging Anderson clusters.

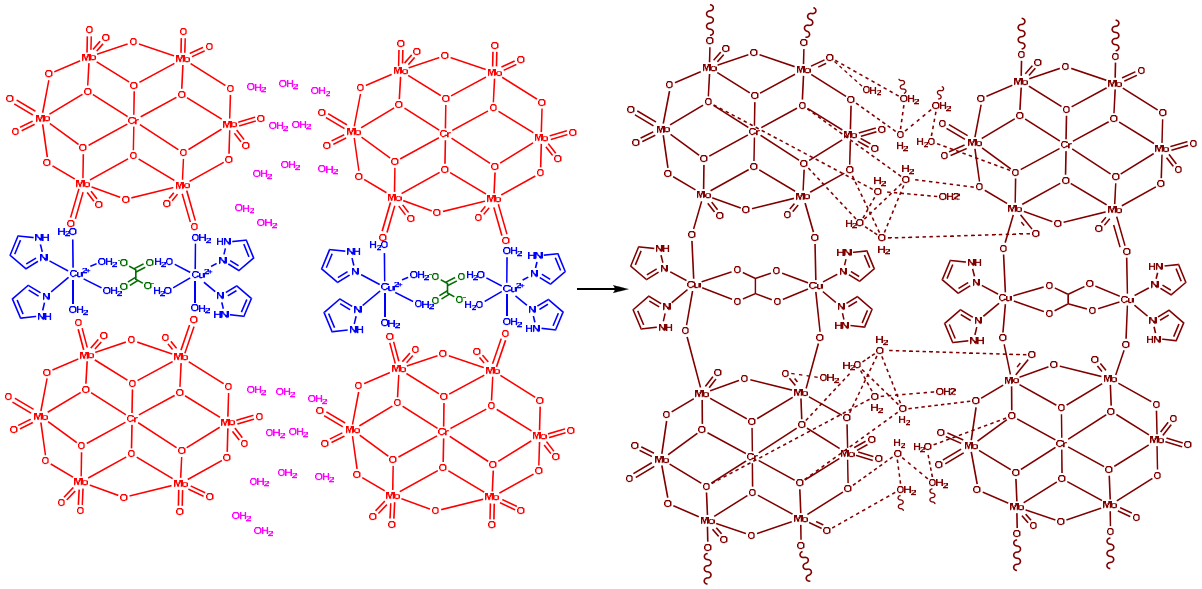


Fig. S5. Crystallization of [{Cu_2(*ox*)(*pz*)$_4$}{$H_7CrMo_6O_{24}$}].11H_2O, **3** occurs from the supramolecular aggregation of the tectons ({$CrMo_6O_{24}$}, oxalate bridged {Cu(*pz*)$_2$(H_2O)$_4$}complex and mediating H_2O molecules for efficient crystal packing. Directionality of self assembly is obvious in terms of supramolecular interactions forming covalently linked 1D chains and nonbonding in the other direction.

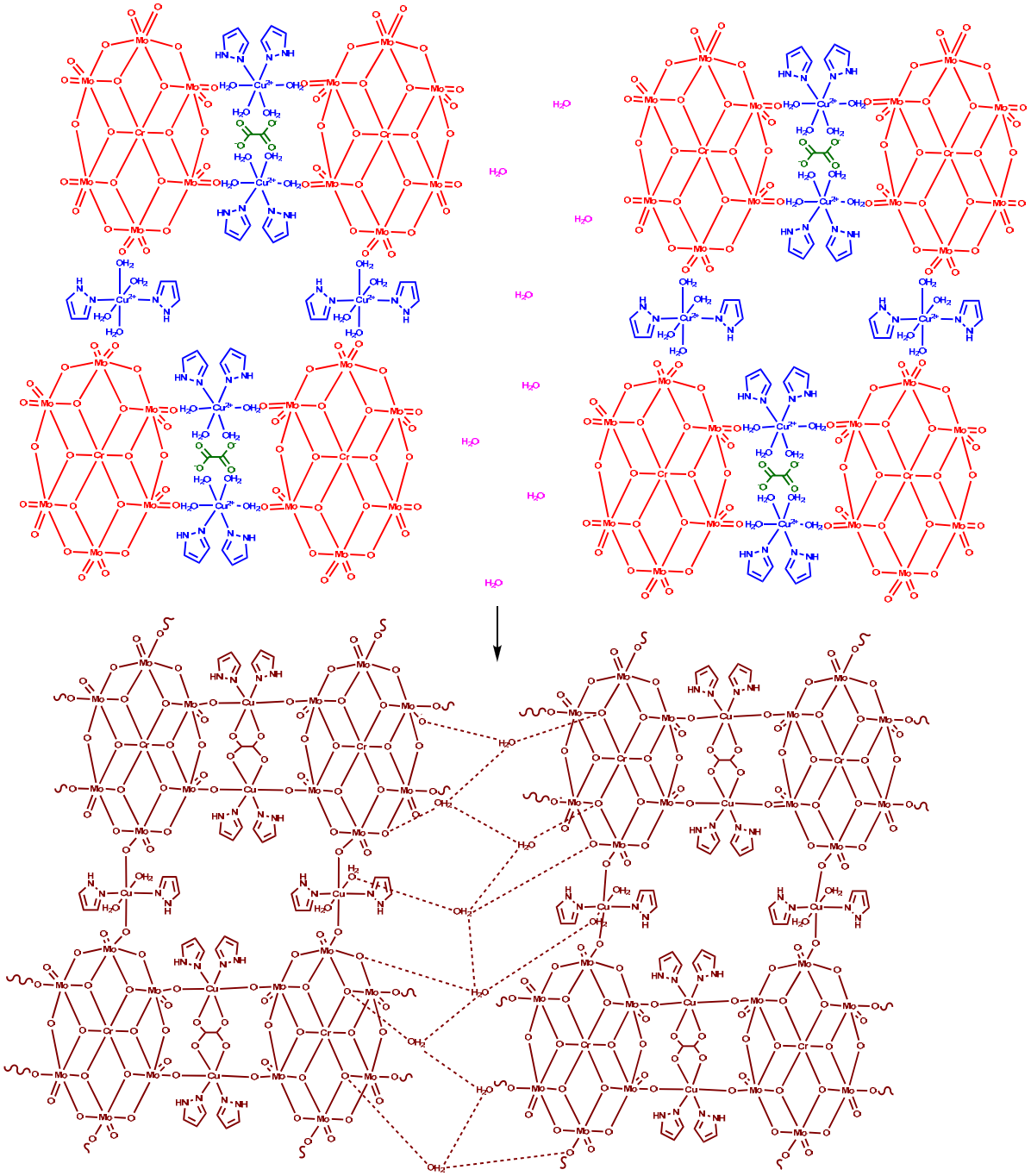


Fig. S6. Crystallization of [{Cu(*pz*)$_2$(H$_2$O)$_2$}{Cu$_2$(*ox*)(*pz*)$_4$}{H$_5$CrMo$_6$O$_{24}$}].8H$_2$O, **4** from the tectons ({CrMo$_6$O$_{24}$}, oxalate bridged copper pyrazole complex and Cu(*pz*)$_2$(H$_2$O)$_4$). Notice the condensation of copper pyrazole complex bridging 1D chains.

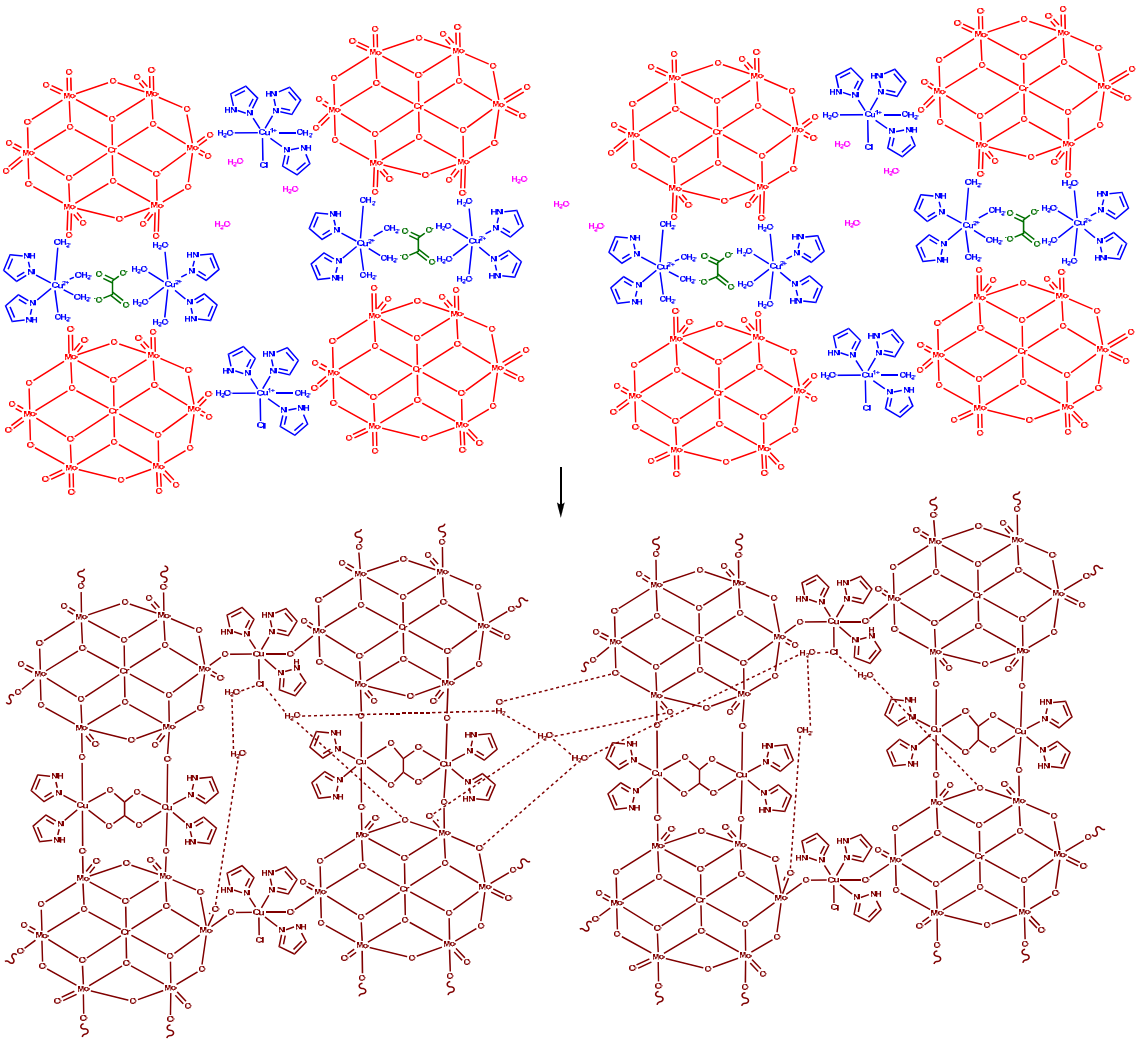


Fig. S7. Crystallization of [{Cu(*pz*)$_3$Cl}{Cu$_2$(*ox*)(*pz*)$_4$}{H$_6$CrMo$_6$O$_{24}$}].8H$_2$O, **5** from the supramolecular assembly of the tectons,{CrMo$_6$O$_{24}$}, oxalate bridged copper pyrazole complex and {Cu(*pz*)$_3$Cl(H$_2$O)$_2$}$^{1+}$. The geometry of tecton bridging 1D chains is different from **4** and hence the chains bend to account for the intermolecular interactions.

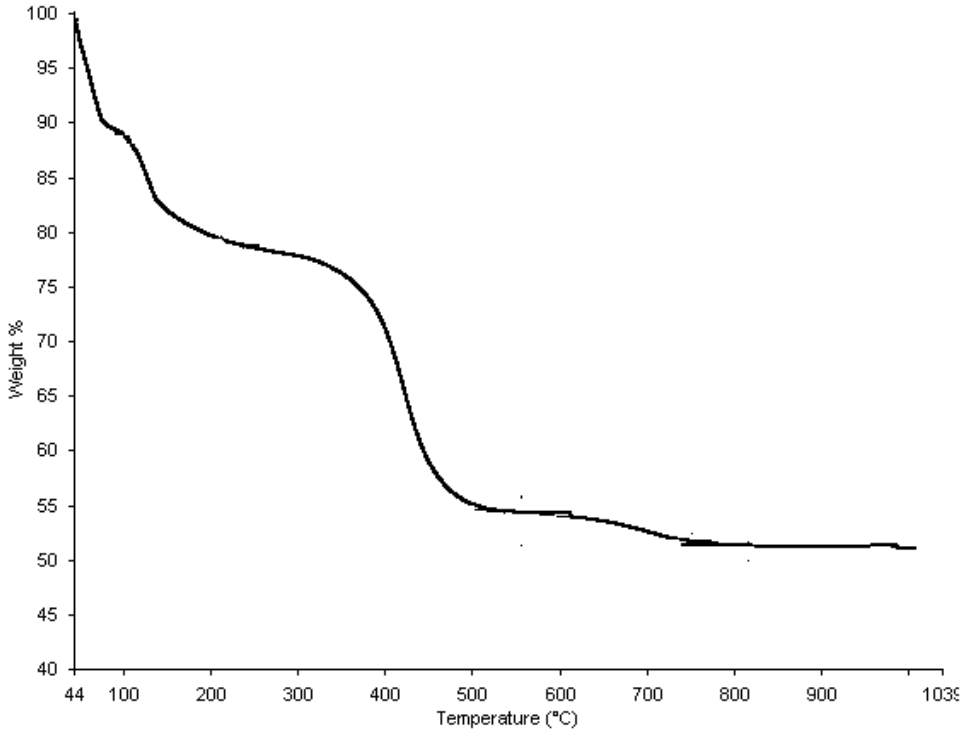


Fig. S8. Thermogravimetric analysis of **1**.

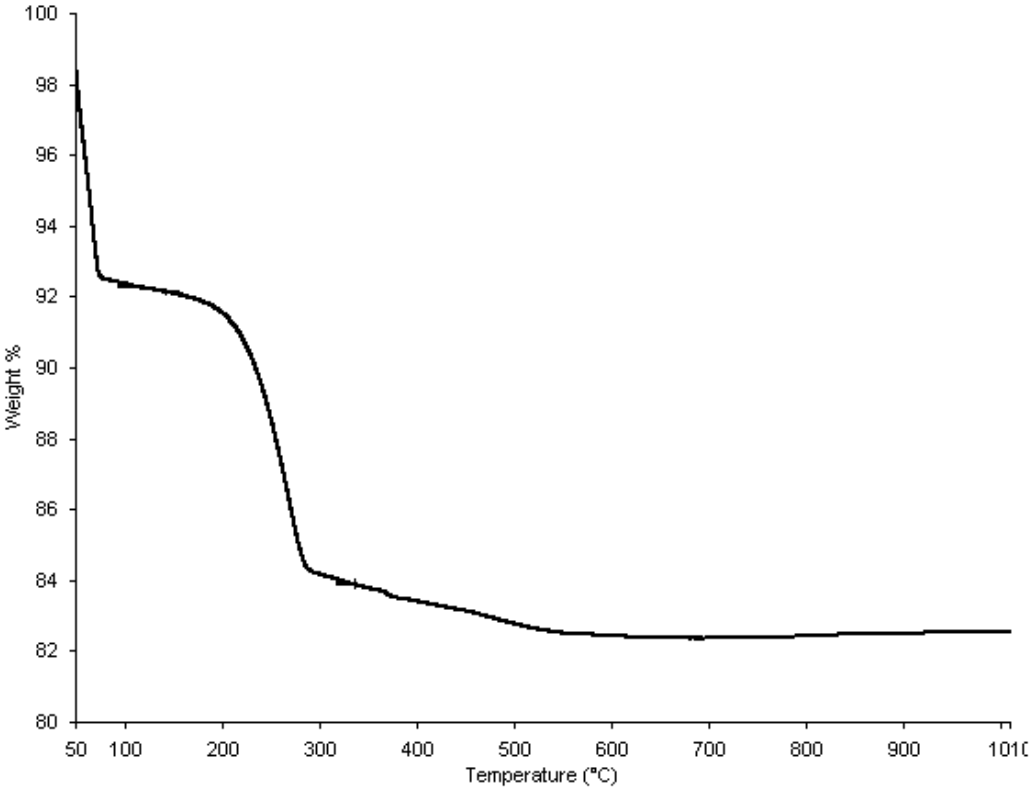


Fig. S9. Thermogravimetric analysis of **2**.

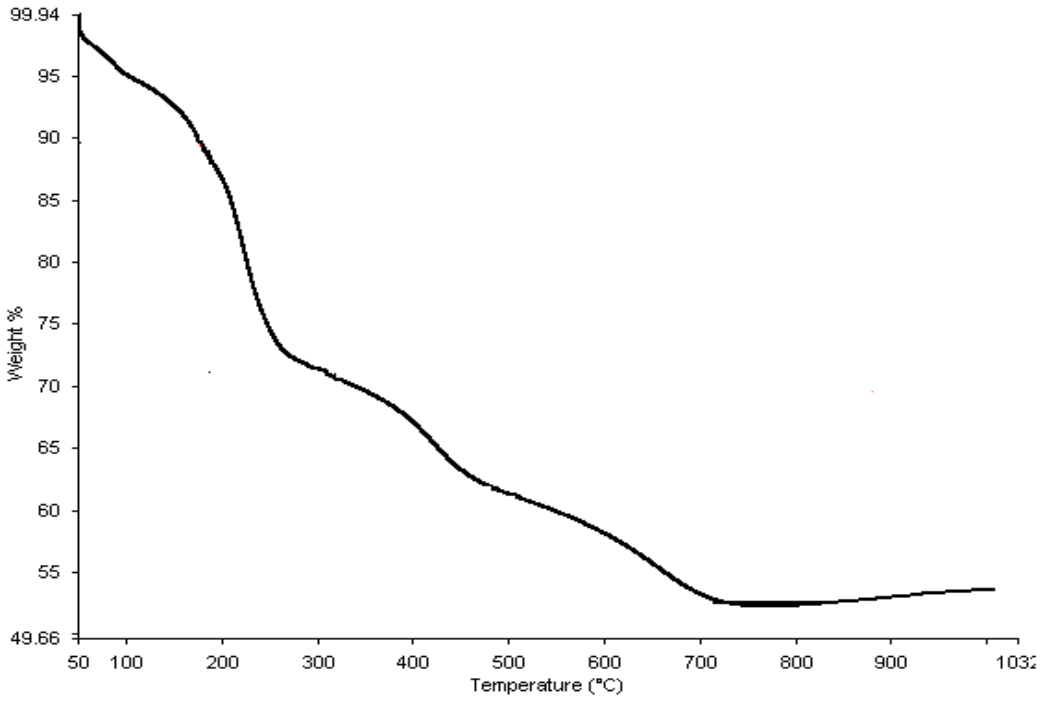


Fig. S10. Thermogravimetric analysis of **3**.

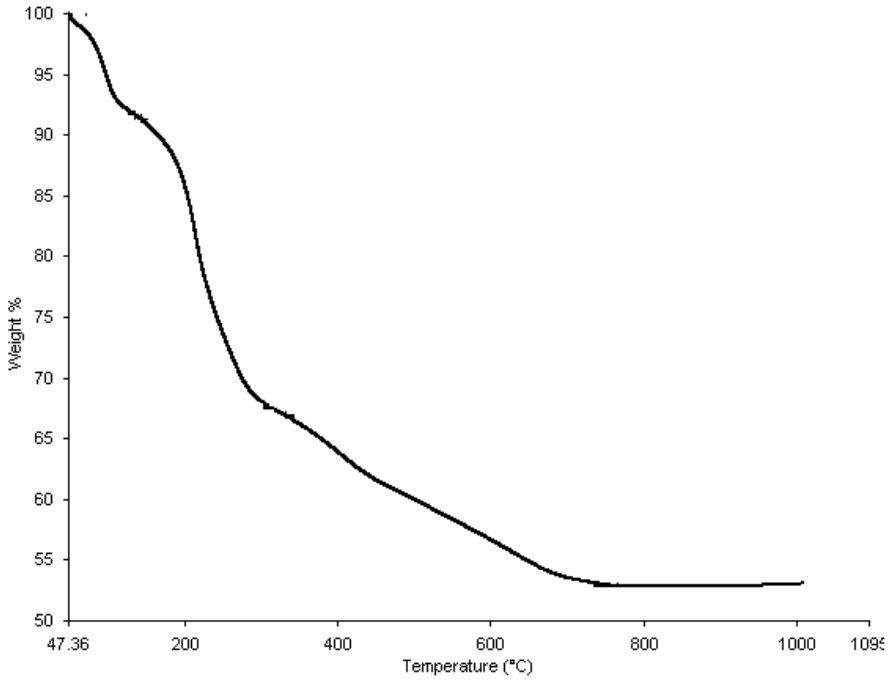


Fig. S11. Thermogravimetric analysis of **4**.

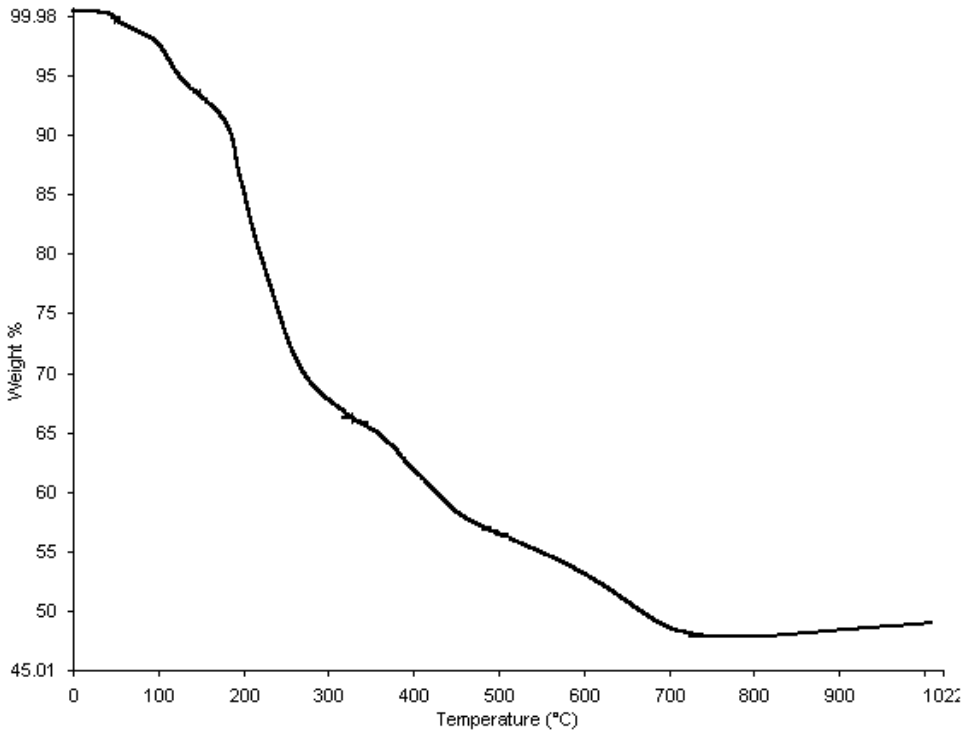


Fig. S12. Thermogravimetric analysis of **5**.

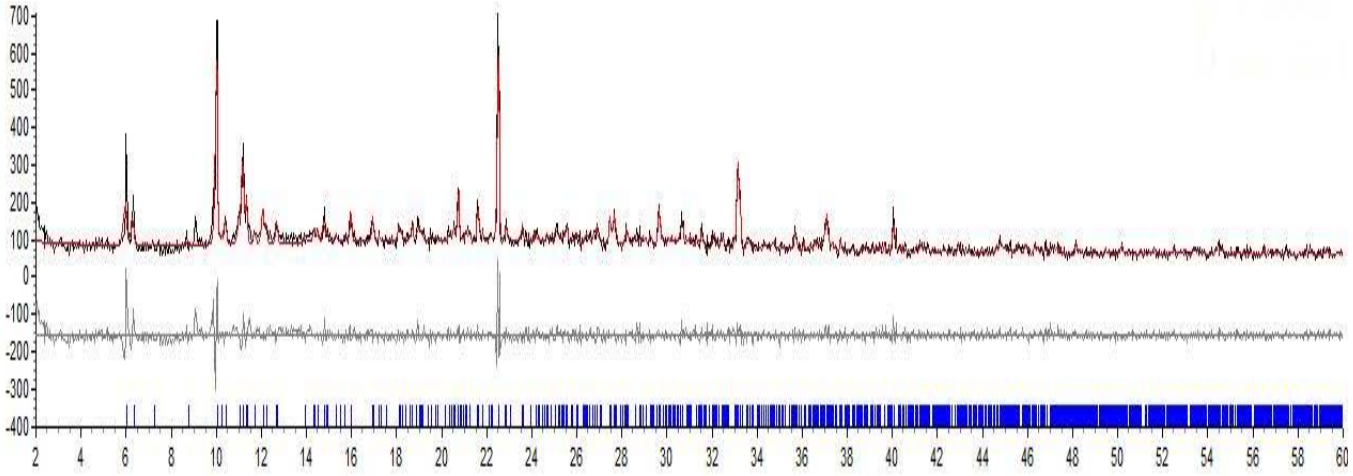


Fig. S13. Reitveld refinement plot for **1**. Rwp = 2.81, Rp = 2.62

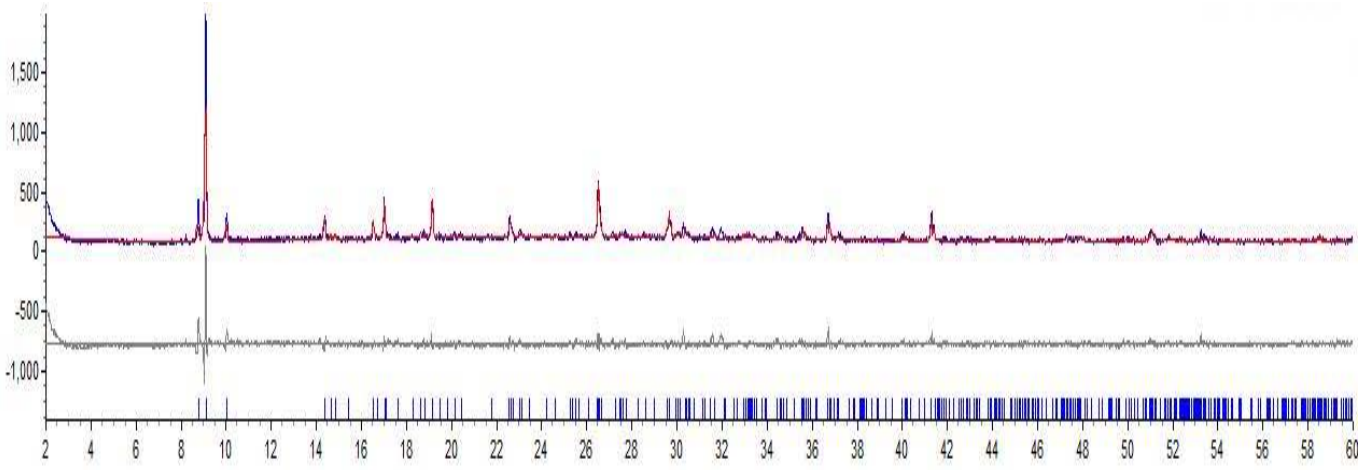


Fig. S14. Reitveld refinement plot for **2**.Rwp = 2.56, Rp = 2.31

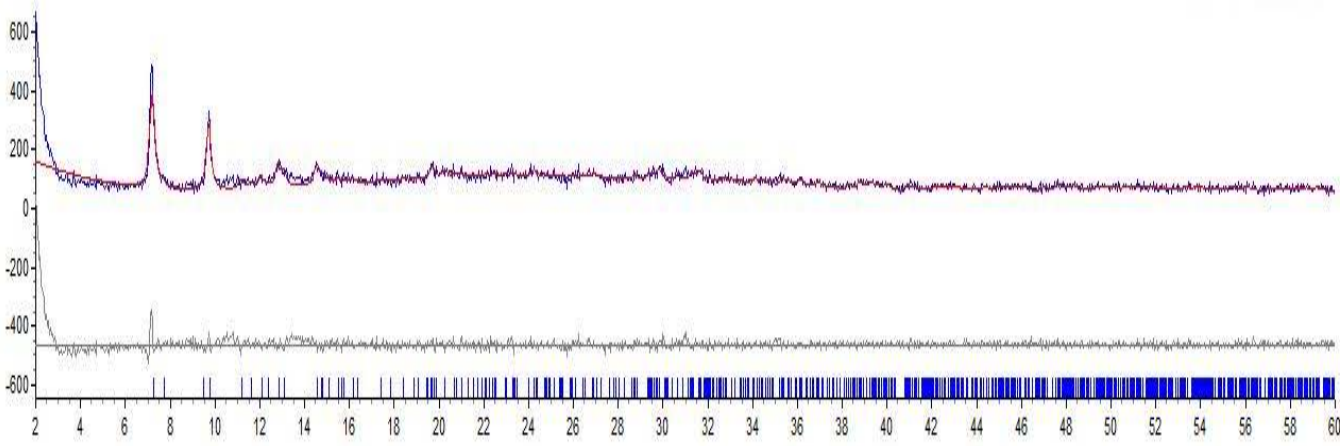


Fig. S15. Reitveld refinement plot for **3**. Rwp = 3.15, Rp = 2.94

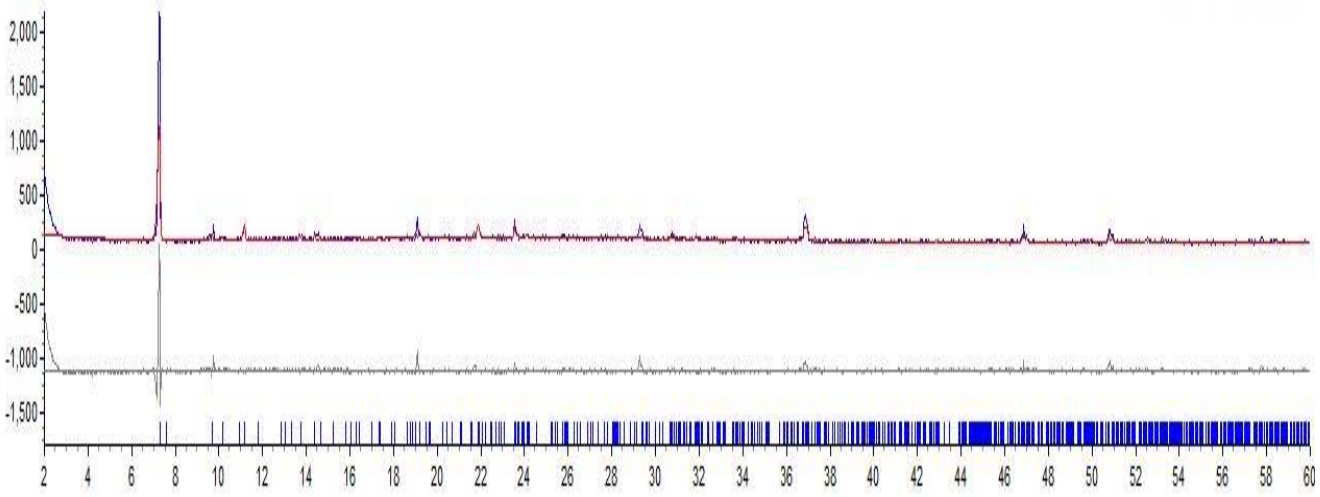


Fig. S16. Reitveld refinement plot for **4**. Rwp = 2.59, Rp = 2.28

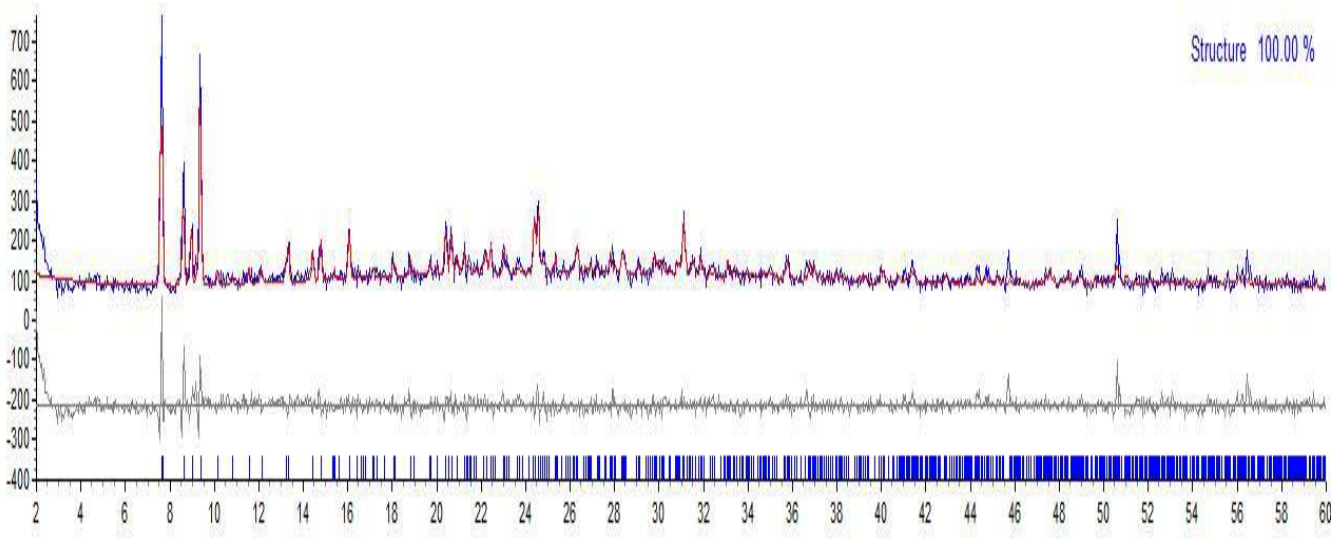


Fig. S17. Reitveld refinement plot for **5**. Rwp = 2.65, Rp = 2.43