

Supplementary Information

Coordination of K^+/Ln^{3+} to Perhydroxycucurbit[5]uril and The Formation of Supramolecular Self-Assemblies in The Presence of $[PMo_{12}O_{40}]^{3-}$ Anions: Potential Application in Isolation of Light Lanthanides

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EXPERIMENTAL SECTION

Synthesis: Chemicals, such as lanthanide nitrates and hydrochloric acid, were of reagent grade and were used without further purification. $(HO)_{10}Q[5]$ was prepared as reported as literature and used as potassium complex form.^{S1} Elemental analyses were carried out on a EURO EA-3000 elemental analyzer. Aqueous HCl ($1.0 \text{ mol}\cdot\text{L}^{-1}$) was used to prepare crystals of $(HO)_{10}Q[5]-Ln(III)$ in the presence of $H_3PMo_{12}O_{40}$. A similar process was used to prepare crystals of related compounds: $(HO)_{10}Q[5]$ (10 mg, 0.0085 mmol) and $Ln(NO_3)_3\cdot xH_2O$ (0.034 mmol, 0.148~0.156 g) were dissolved in 1.0 mL $1.0 \text{ mol}\cdot\text{L}^{-1}$ HCl (solution A), $H_3PMo_{12}O_{40}$ was dissolved in 1.0 mL $1.0 \text{ mol}\cdot\text{L}^{-1}$ HCl (solution B), and was then added in the solution A with stirring for the $Ln-(HO)_{10}Q[5]-[PMo_{12}O_{40}]^{3-}$ systems. X-ray quality crystals were obtained from the solution over a period of 1-5 days. The yellowish-green granular crystals were dependent on the lanthanide ions. Summarizing the preparations according to the three isomorphous groups: $\{K(H_2O)_2Ln(H_2O)_3Cl@HO_{10}Q[5]\}\cdot [PMo_{12}O_{40}]\cdot 13H_2O$ (**1,2**, Ln = La, Ce) for the first isomorphous group, except compound **3** with a

formula of $\text{Pr}(\text{H}_2\text{O})_3\text{Cl}@\text{HO}_{10}\text{Q}[5]\cdot[\text{PMo}_{12}\text{O}_{40}]\cdot\text{H}_3\text{O}\cdot 15\text{H}_2\text{O}$; $\{\text{K}(\text{H}_2\text{O})\text{Ln}(\text{H}_2\text{O})_2(\text{Cl}@\text{HO}_{10}\text{Q}[5])\}[\text{PMo}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ (**4,6,7**, Ln = Nd, Sm, Eu, $11 \leq x \leq 13$) for the second isomorphous group; the compound **8** with a formula of $\{\text{K}(\text{H}_2\text{O})\text{Gd}(\text{H}_2\text{O})_2\text{Cl}@\text{HO}_{10}\text{Q}[5]\}[\text{PMo}_{12}\text{O}_{40}]\cdot 11\text{H}_2\text{O}$ shows similar coordination to those in the first two isomorphous groups, and supramolecular assembly to those in the third isomorphous group; $\{\text{K}_2(\text{H}_2\text{O})_2(\text{NO}_3@\text{HO}_{10}\text{Q}[5])\}[\text{PMo}_{12}\text{O}_{40}]\cdot 2\text{H}_3\text{O}\cdot x\text{H}_2\text{O}$ (**9~12**, Ln = Tb, Dy, Ho, Er, $10 \leq x \leq 11$) and $\{\text{K}_2(\text{H}_2\text{O})_2(\text{H}_2\text{O}@\text{HO}_{10}\text{Q}[5])\}[\text{PMo}_{12}\text{O}_{40}]\cdot \text{H}_3\text{O}\cdot x\text{H}_2\text{O}$ (**13~15**, Ln = Tm, Yb, Lu, $12 \leq x \leq 13$) for the third isomorphous group. Elemental analysis results for the eleven compounds are given in Table 1.

Table 1. Elemental Analysis Results (%)

Results	1-La	2-Ce	3-Pr	4-Nd	6-Sm	7-Eu	8-Gd
C calcd.	10.75	10.75	10.81	10.74	10.95	10.95	10.93
found	10.89	10.81	10.88	10.85	11.05	11.10	11.21
H calcd.	1.99	1.98	2.09	1.86	1.78	1.78	1.77
found	1.91	1.90	2.00	1.77	1.67	1.71	1.69
N calcd.	8.36	8.36	8.41	8.35	8.51	8.51	8.50
found	8.40	8.51	8.33	8.41	8.60	8.68	8.62
Results	9-Tb	10-Dy	11-Ho	12-Er	13-Tm	14-Yb	15-Lu
C calcd.	11.23	11.22	11.17	11.17	11.33	11.39	11.39
found	11.34	11.29	11.23	11.33	11.51	11.52	11.49
H calcd.	1.89	1.95	1.94	1.94	2.00	1.94	1.94
found	1.85	2.07	2.07	2.11	2.08	2.09	2.12
N calcd.	9.17	8.72	9.12	9.12	8.81	8.86	8.86
found	9.27	8.79	9.21	9.16	8.90	9.00	8.97

X-ray crystallography: A suitable single crystal ($\sim 0.2 \times 0.2 \times 0.1 \text{ mm}^3$) was taken up in paraffin oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo- K_α ($\lambda = 0.71073 \text{ \AA}$, $\mu = 0.828 \text{ mm}^{-1}$) radiation source operating in the ω -scan mode and a nitrogen cold stream (-50 C). Data were corrected for Lorentz and polarization effects (SAINT),^{S2} and semi-empirical absorption corrections based on equivalent reflections were also applied (SADABS).^{S2} The structure was elucidated by direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXS-97 and SHELXL-97 program packages, respectively.^{S3} All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were introduced at calculated positions, and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Most of the water molecules in the

compounds were omitted using the SQUEEZE option of the PLATON program, except the coordinated water molecules. The squeezed water molecules are 10, 10, 14, 12, and 9, 9, 9, 10, 10, 9, 11, 11, 10, 8 for compounds **1-4**, **6-15**, respectively. For compounds 9-15, the phosphate moiety of the anion is disordered by symmetry. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Details of the crystal parameters, data collection conditions, and refinement parameters for the fourteen compounds are summarized in Table 2. In addition, the crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-964173 (**1**), 964174 (**2**), 964175 (**3**), 964176 (**4**), 964177 (**6**), 964178 (**7**), 964179 (**8**), 964180 (**9**), 964181 (**10**), 964182 (**11**), 964183 (**12**), 964184 (**13**), 964185(**14**), 964186(**15**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Reference

- S1 S. Y. Jon, N. Selvapalam, D. H. Oh, J. K. Kang, S. Y. Kim, Y. J. Jeon, J. W. Lee and K. Kim, *J. Am. Chem. Soc.*, 2003, **125**, 10186.
 S2 Bruker. *SAINTE* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA. 2005.
 S3 (a) SHELXTL program package, version 5.1; Bruker AXS, Inc.: Madison, WI. (b) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

Table 2-1. Crystal Data and Structure Refinement Details for Compounds

Compound	1-La	2-Ce	3-Pr	4-Nd	6-Sm	7-Eu	8-Gd
Empirical formula	C ₃₀ H ₆₆ ClKLa Mo ₁₂ N ₂₀ O ₇₈ P	C ₃₀ H ₆₆ ClKCe Mo ₁₂ N ₂₀ O ₇₈ P	C ₃₀ H ₆₉ ClPr Mo ₁₂ N ₂₀ O ₇₉ P	C ₃₀ H ₆₂ ClKNd Mo ₁₂ N ₂₀ O ₇₆ P	C ₃₀ H ₅₈ ClKSm Mo ₁₂ N ₂₀ O ₇₄ P	C ₃₀ H ₅₈ ClKEu Mo ₁₂ N ₂₀ O ₇₄ P	C ₃₀ H ₅₈ ClKGd Mo ₁₂ N ₂₀ O ₇₄ P
Formula weight	3350.74	3351.95	3332.66	3320.04	3290.11	3291.72	3297.01
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	P c a 21	P c a 21	P c a 21	P n m a	P n m a	P n m a	P n m a
a, Å	46.552(13)	46.525(7)	46.551(5)	22.648(4)	22.655(13)	22.524(4)	22.485(3)
b, Å	15.749(4)	15.707(2)	15.6964(17)	15.759(3)	15.874(9)	15.876(3)	15.879(2)
c, Å	22.925(6)	22.889(3)	22.913(3)	23.177(4)	23.210(13)	23.193(4)	23.163(3)
α, deg	90	90	90	90	90	90	90
β, deg	90	90	90	90	90	90	90
γ, deg	90	90	90	90	90	90	90
V, Å ³	16807(8)	16726(4)	16742(3)	8272(3)	8347(8)	8293(3)	8270(2)
Z	8	8	8	4	4	4	4

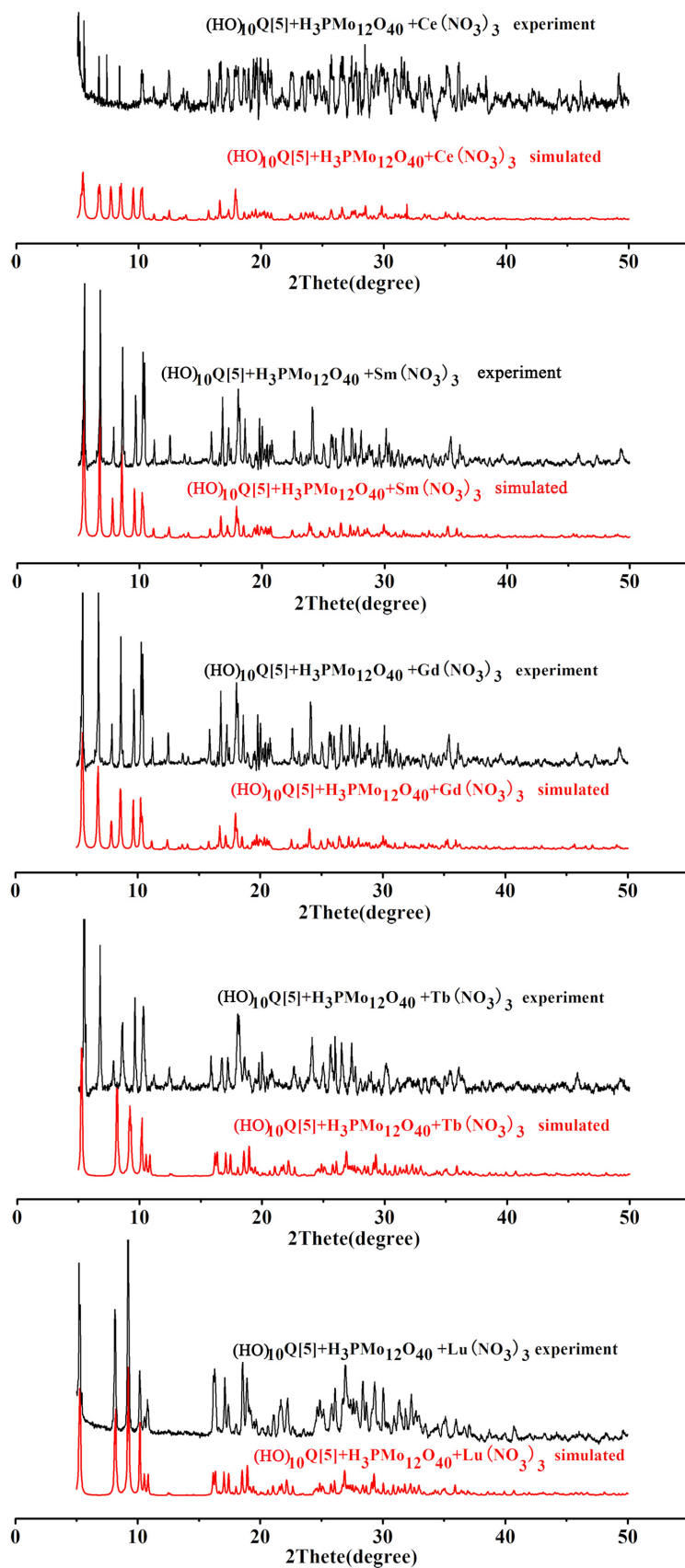
Dcalcd, g cm ⁻³	2.648	2.662	2.644	2.666	2.618	2.636	2.648
T, K	223(2)	223	223	223	223	223	223
μ, mm ⁻¹	2.468	2.513	2.501	2.615	2.670	2.735	2.787
Unique reflns	29812	28977	29635	7638	7638	7644	7643
Obsd reflns	25025	24789	20924	5405	5277	5120	5333
Params	2422	2347	2167	619	624	624	627
Rint	0.0757	0.0659	0.0966	0.0889	0.0694	0.0695	0.0658
R[I > 2σ(I)] ^a	0.0490	0.0476	0.0564	0.0831	0.0648	0.0628	0.0587
wR[I > 2σ(I)] ^b	0.1140	0.1070	0.1245	0.2169	0.1748	0.1618	0.1553
R(all data)	0.0602	0.0582	0.0835	0.1094	0.0913	0.0932	0.0834
wR(all data)	0.1203	0.1130	0.1357	0.2369	0.1914	0.1773	0.1691
GOF on F ²	1.037	1.036	1.015	1.091	1.118	1.086	1.109

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum w(|F_o|^2 - |F_c|^2) / \sum w(F_o)^2]^{1/2}, \quad \text{where } w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]; \quad P = (F_o^2 + 2F_c^2) / 3.$$

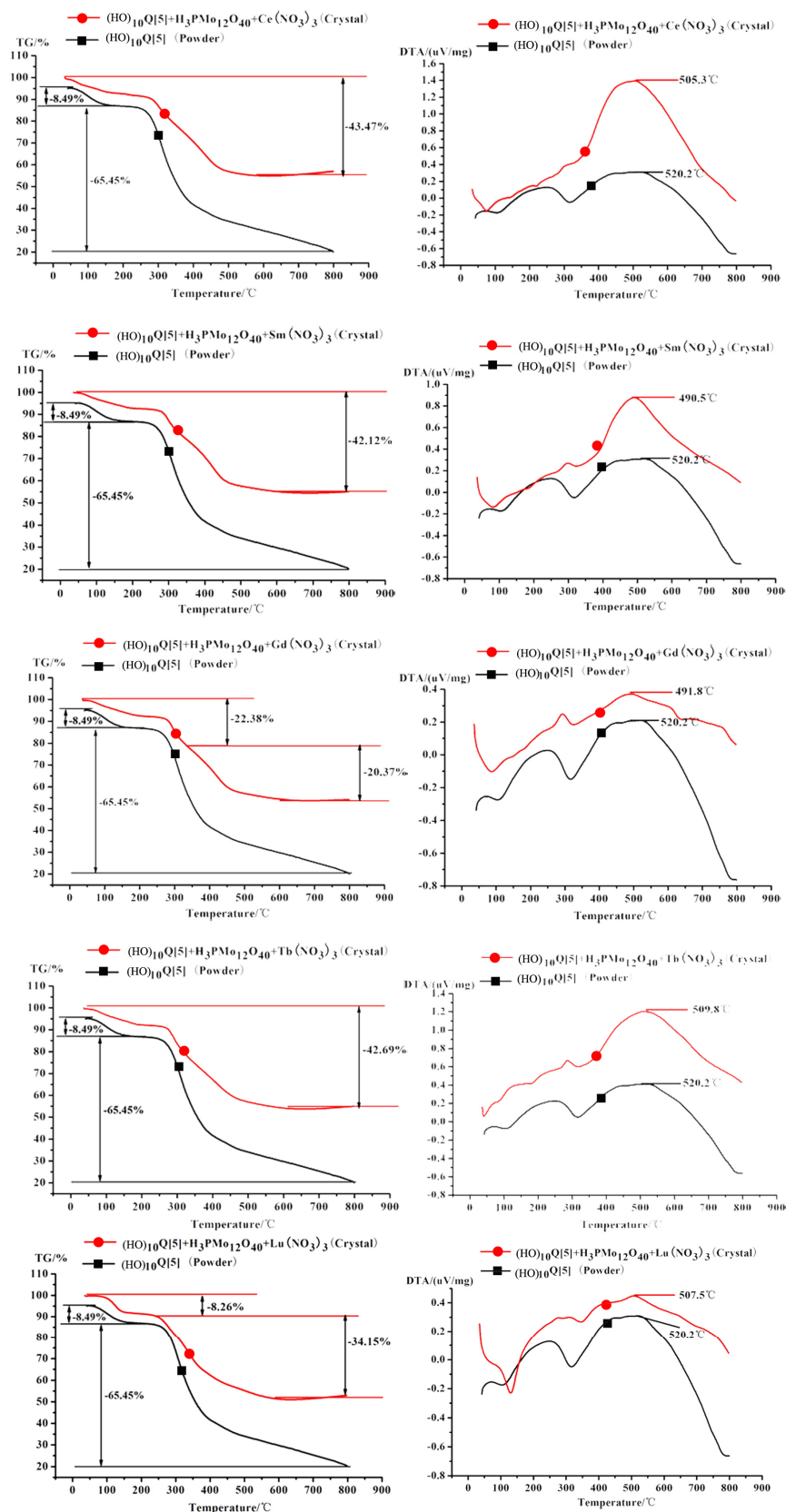
Table 2-2. Crystal Data and Structure Refinement Details for Compounds

Compound	9-Tb	10-Dy	11-Ho	12-Er	13-Tm	14-Yb	15-Lu
Empirical formula	C ₃₀ H ₆₀ K ₂ Mo ₁₂ N ₂₁ O ₇₇ P	C ₃₀ H ₆₂ K ₂ Mo ₁₂ N ₂₁ O ₇₈ P	C ₃₀ H ₆₂ K ₂ Mo ₁₂ N ₂₁ O ₇₈ P	C ₃₀ H ₆₂ K ₂ Mo ₁₂ N ₂₁ O ₇₈ P	C ₃₀ H ₆₃ K ₂ Mo ₁₂ N ₂₀ O ₇₆ P	C ₃₀ H ₆₁ K ₂ Mo ₁₂ N ₂₀ O ₇₅ P	C ₃₀ H ₆₁ K ₂ Mo ₁₂ N ₂₀ O ₇₅ P
Formula weight	3207.44	3225.46	3225.46	3225.46	3180.45	3162.44	3162.44
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C 2/c	C 2/c	C 2/c	C 2/c	C 2/c	C 2/c	C 2/c
a, Å	16.5175(13)	16.4852(11)	16.4880(7)	16.536(2)	16.5232(15)	16.622(2)	16.543(2)
b, Å	14.4895(12)	14.4496(9)	14.4729(6)	14.4599(18)	14.4587(12)	14.5029(19)	14.4575(18)
c, Å	33.998(3)	33.998(2)	33.9442(13)	33.916(4)	33.985(3)	33.980(5)	33.922(4)
α, deg	90	90	90	90	90	90	90
β, deg	99.206(2)	99.185(2)	99.196(2)	99.140(4)	99.026(3)	98.924(4)	99.052(4)
γ, deg	90	90	90	90	90	90	90
V, Å ³	8031.9(11)	7994.6(9)	7996.0(6)	8006.5(17)	8018.6(12)	8092.2(18)	8011.8(17)
Z	4	4	4	4	4	4	4
Dcalcd, g cm ⁻³	2.652	2.680	2.679	2.676	2.634	2.596	2.622
T, K	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)
μ, mm ⁻¹	2.082	2.093	2.093	2.090	2.083	2.062	2.083
Unique reflns	6964	7159	9057	7771	7012	7157	6995
Obsd reflns	4589	5884	6856	5744	4620	6115	5288
Params	602	607	611	592	590	606	591
Rint	0.0811	0.0583	0.0571	0.0614	0.0861	0.0512	0.0631

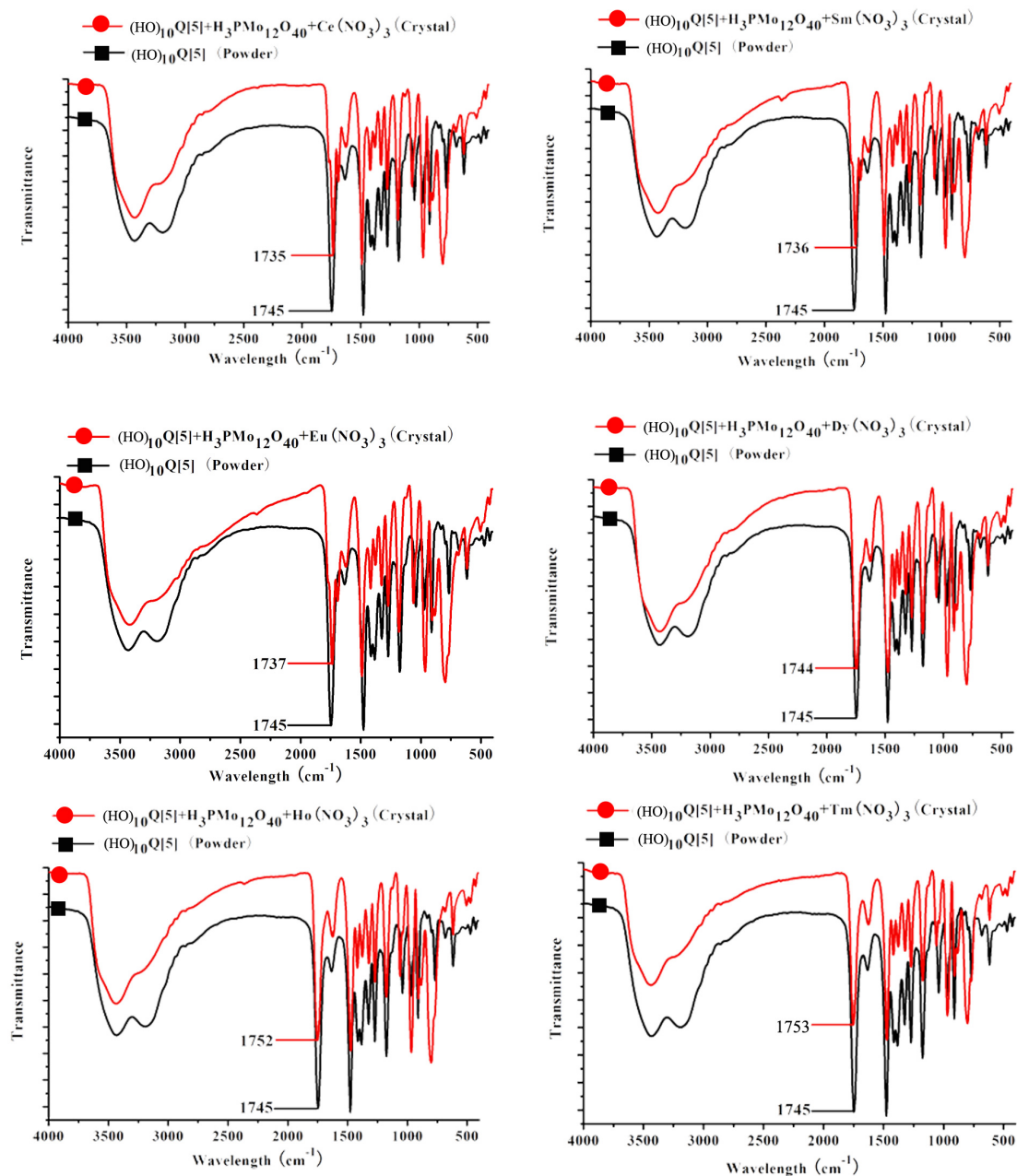
$R[I > 2\sigma(I)]^a$	0.0657	0.0608	0.0557	0.0531	0.0688	0.0489	0.0649
$wR[I > 2\sigma(I)]^b$	0.1736	0.1457	0.1388	0.1381	0.1930	0.1439	0.1967
R(all data)	0.0950	0.0719	0.0756	0.0749	0.1025	0.0561	0.0842
wR(all data)	0.1950	0.1516	0.1497	0.1520	0.2092	0.1482	0.2190
GOF on F2	1.056	1.051	1.065	1.093	1.077	1.094	1.077



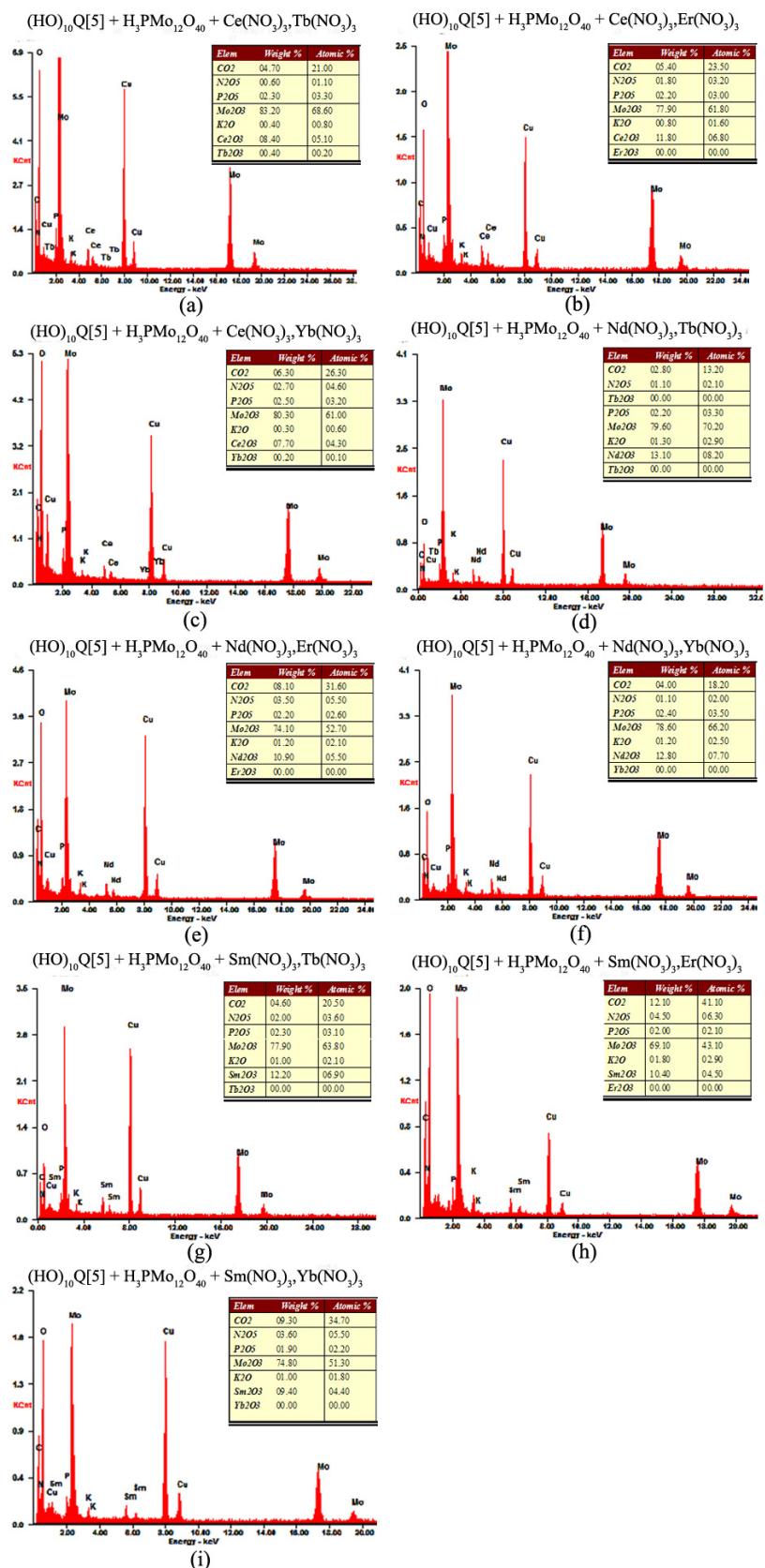
SI-Fig. 1 Powder X-ray diffraction (PXRD) of the representative crystals from the three isomorphous groups respectively



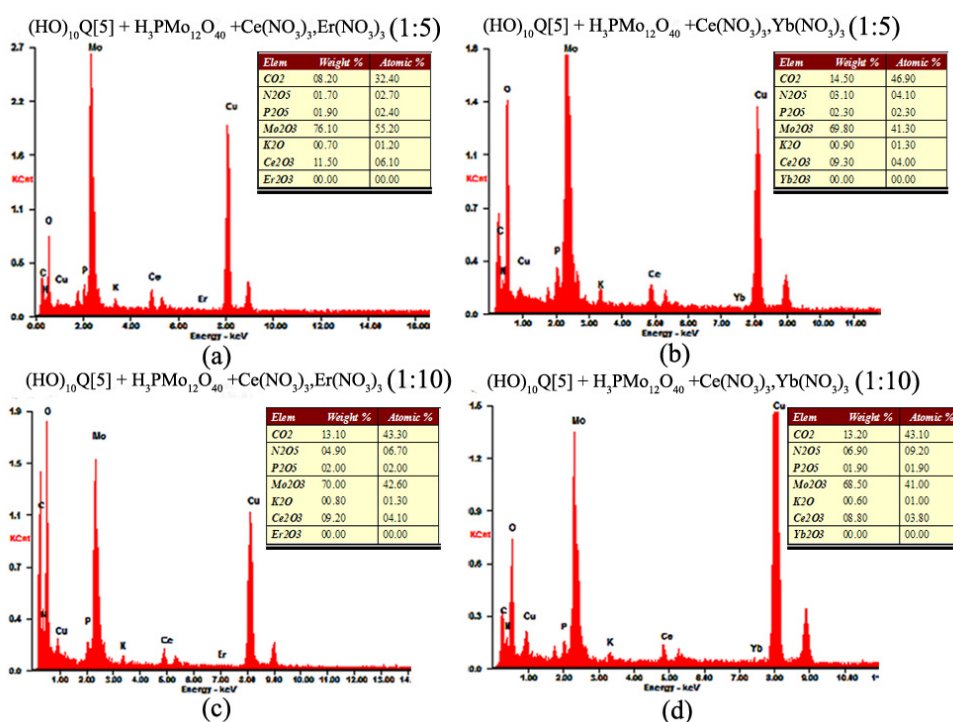
SI-Fig. 2 TG (left) and DSC (right) curves of the representative crystals from the three isomorphous groups with a comparison of (HO)₁₀Q[5] in N₂ respectively



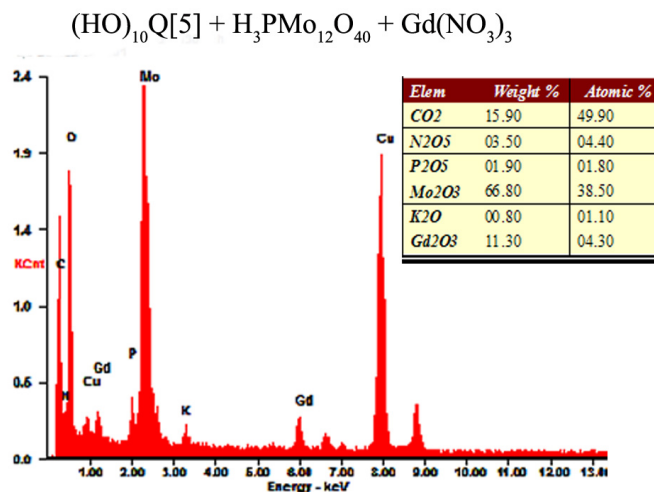
SI-Fig. 3 FT-IR spectra of the representative crystals from the three isomorphous groups with a comparison of (HO)₁₀Q[5] powders respectively.



SI-Fig. 4 the electron spectroscopy of $\text{K}^+(\text{HO})_{10}\text{Q}[5]/[\text{PMo}_{12}\text{O}_{40}]^{3-}$ systems with 1:1 ratios of light : heavy lanthanides



SI-Fig. 5 the electron spectroscopy of $\text{K}^+(\text{HO})_{10}\text{Q}[5]/[\text{PMo}_{12}\text{O}_{40}]^{3-}$ systems with 1:5 and 1:10 ratios of light : heavy lanthanides



SI-Fig. 6 the electron spectroscopy of the compound 8.