Table S1. Fractional atomic coordinates and coefficients of the equivalent isotropic displacement parameters for $(N_2H_5)_3[NO_3][B_{12}H_{12}] \cdot H_2O$ (**I**).

Atom	*Wyckoff* site	*x / a*	*y / b*	*z / c*	U_{eq} / pm^2
N0	4*a*	0	0.05974(17)	0.0000(3)	278(7)
O1	4*a*	0	0.12741(17)	0.9929(4)	521(9)
O2	4*a*	0	0.02175(18)	0.8909(4)	486(9)
O3	4*a*	0	0.02989(17)	0.1190(3)	426(7)
B1	4*a*	0	0.4641(2)	0.2151(5)	251(8)
H1	4*a*	0	0.524	0.200	389(126)
B2	4*a*	0	0.4025(2)	0.0703(4)	236(8)
H2	4*a*	0	0.423	–0.039	751(22)
B3	4*a*	0	0.3410(2)	0.4054(5)	260(8)
H3	4*a*	0	0.321	0.514	142(86)
B4	4*a*	0	0.2791(2)	0.2592(4)	244(8)
H4	4*a*	0	0.219	0.273	104(24)
B5	8*b*	0.0935(3)	0.42158(15)	0.3558(3)	239(5)
H5	8*b*	0.156	0.454	0.432	983(167)
B6	8*b*	0.1508(3)	0.40966(15)	0.1790(3)	244(5)
H6	8*b*	0.252	0.435	0.140	126(58)
B7	8*b*	0.1518(3)	0.33334(16)	0.2970(3)	265(6)
H7	8*b*	0.254	0.308	0.336	734(148)
B8	8*b*	0.0943(3)	0.32134(15)	0.1208(3)	263(6)
H8	8*b*	0.158	0.289	0.045	295(82)
N1	4*a*	0	0.1295(2)	0.6706(4)	354(8)
H11	4*a*	0	0.079(3)	0.678(6)	425*
H12	8*b*	0.072(4)	0.153(2)	0.712(4)	425*
N2	4*a*	0	0.1554(2)	0.5294(4)	353(8)
H21	8*b*	0.075(4)	0.148(2)	0.517(4)	423*
N3	8*b*	0.2149(3)	0.0929(2)	0.3145(3)	424(6)
N31	8*b*	0.160(5)	0.055(2)	0.266(4)	509*
N32	8*b*	0.154(5)	0.112(2)	0.380(4)	509*
N33	8*b*	0.305(4)	0.062(2)	0.356(4)	509*
N4	8*b*	0.2668(3)	0.1370(2)	0.2025(4)	491(7)
N41	8*b*	0.238(5)	0.160(2)	0.173(5)	590*
N42	8*b*	0.285(5)	0.104(2)	0.132(5)	590*
Ow	4*a*	0	0.7243(2)	0.2814(4)	460(9)
Hw	8*b*	–0.042(5)	0.701(2)	0.265(5)	552*

* The factor is 1.2, i.e., fixed to the value of 1.2 times that of the displacement factor of the above-mentioned covalent bonding heavy atoms (oxygen and nitrogen atoms).

Table S2. Fractional atomic coordinates and coefficients of the equivalent isotropic displacement parameters for $[N_2H_5]_3[ClO_4][B_{12}H_{12}] \cdot H_2O$ (**II**).

Atom	*Wyckoff* site	*x / a*	*y / b*	*z / c*	U_{eq} / pm^2
Cl0	4*a*	0	0.05877(4)	0.00000(8)	353(2)
O1	4*a*	0	0.1365(2)	0.9766(5)	986(14)
O2	4*a*	0	0.0406(2)	0.1472(4)	864(12)
O3	8*b*	0.1091(2)	0.02467(17)	0.9358(3)	804(8)
B1	4*a*	0	0.4597(2)	0.7395(4)	394(10)
H1	4*a*	0	0.518(2)	0.749(4)	408(110)
B2	4*a*	0	0.3966(2)	0.8861(4)	402(10)
H2	4*a*	0	0.420(2)	0.981(6)	617(132)
B3	4*a*	0	0.3319(2)	0.5510(4)	350(9)
H3	4*a*	0	0.313(3)	0.446(6)	716(155)
B4	4*a*	0	0.2684(2)	0.6993(4)	343(9)
H4	4*a*	0	0.208(2)	0.696(4)	402(105)
B5	8b	0.0847(3)	0.41499(17)	0.5993(3)	379(7)
H5	8*b*	0.137(2)	0.4500(15)	0.525(3)	408(73)
B6	8*b*	0.1378(3)	0.40401(18)	0.7774(3)	417(7)
H6	8*b*	0.229(3)	0.4351(18)	0.820(4)	643(105)
B7	8*b*	0.1395(3)	0.32435(16)	0.6604(3)	354(6)
H7	8*b*	0.235(3)	0.2953(18)	0.622(4)	638(92)
B8	8*b*	0.0855(3)	0.31292(16)	0.8384(3)	343(6)
H8	8*b*	0.140(2)	0.28787(16)	0.922(3)	385(69)
N1	8*b*	0.2714(4)	0.4132(2)	0.1515(3)	699(10)
H11	8*b*	0.297(5)	0.399(3)	0.090(6)	839*
H12	8*b*	0.218(5)	0.431(3)	0.117(6)	839*
H13	8*b*	0.350(4)	0.452(2)	0.195(4)	839*
N2	8*b*	0.2227(3)	0.36329(2)	0.2558(3)	628(8)
H21	8*b*	0.273(4)	0.338(3)	0.269(5)	753*
H22	8*b*	0.197(4)	0.390(2)	0.329(5)	753*
N3	8*b*	0.4320(5)	0.3474(2)	0.9120(5)	107(2)
H31	8*b*	0.402(5)	0.330(3)	0.835(7)	128*
H32	8*b*	0.445(5)	0.391(3)	0.852(6)	128*
H33	8*b*	0.415(5)	0.337(3)	1.011(6)	128*
Ow	4*a*	0.0000	0.2696(2)	0.1872(3)	81(2)
Hw	8*b*	0.021(6)	0.263(2)	0.127(5)	967*

* The factor is 1.2, i.e., fixed to the value of 1.2 times that of the displacement factor of the above-mentioned covalent bonding heavy atoms (oxygen and nitrogen atoms); one of the sites for the H31, H32, or H33 atoms should only be half-occupied.

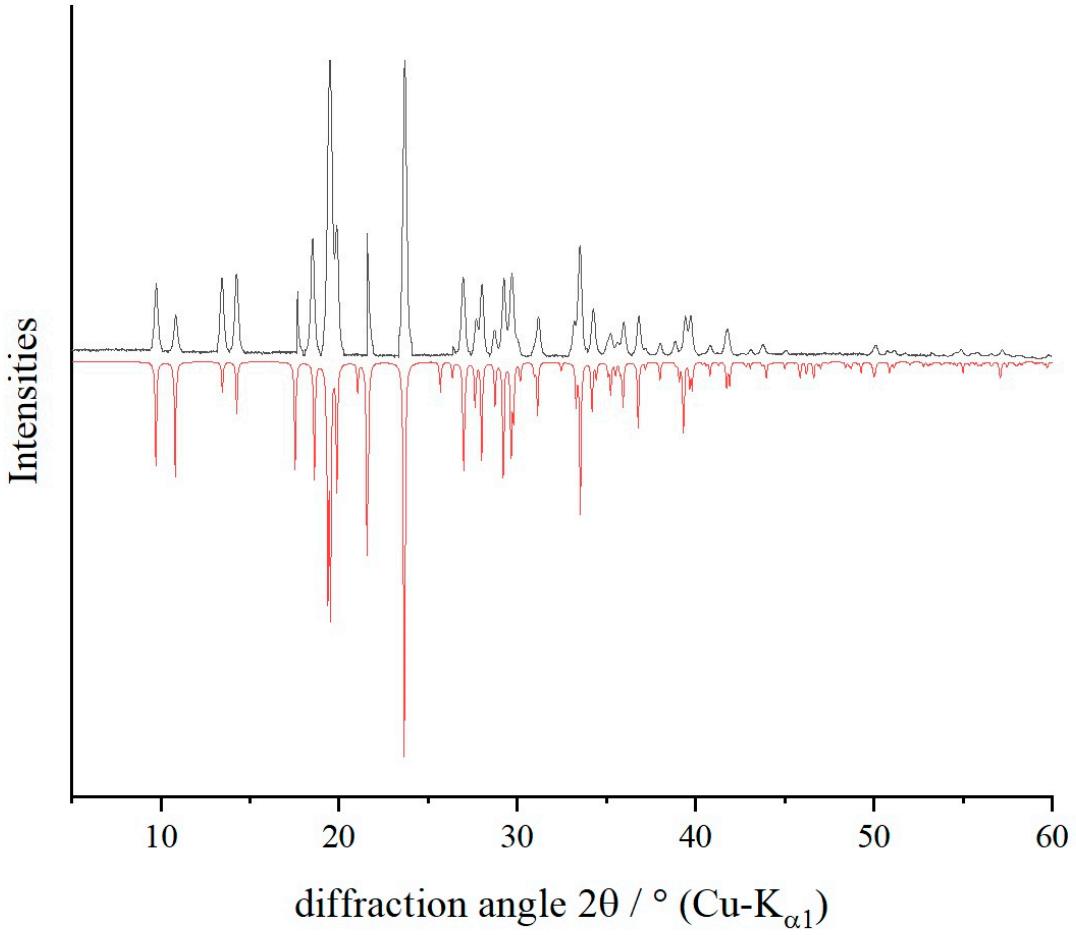

Figure S1. Powder X-ray diffraction pattern of $(N_2H_5)_3[NO_3][B_{12}H_{12}] \cdot H_2O$ (**I**) (top) and the calculated pattern (bottom).

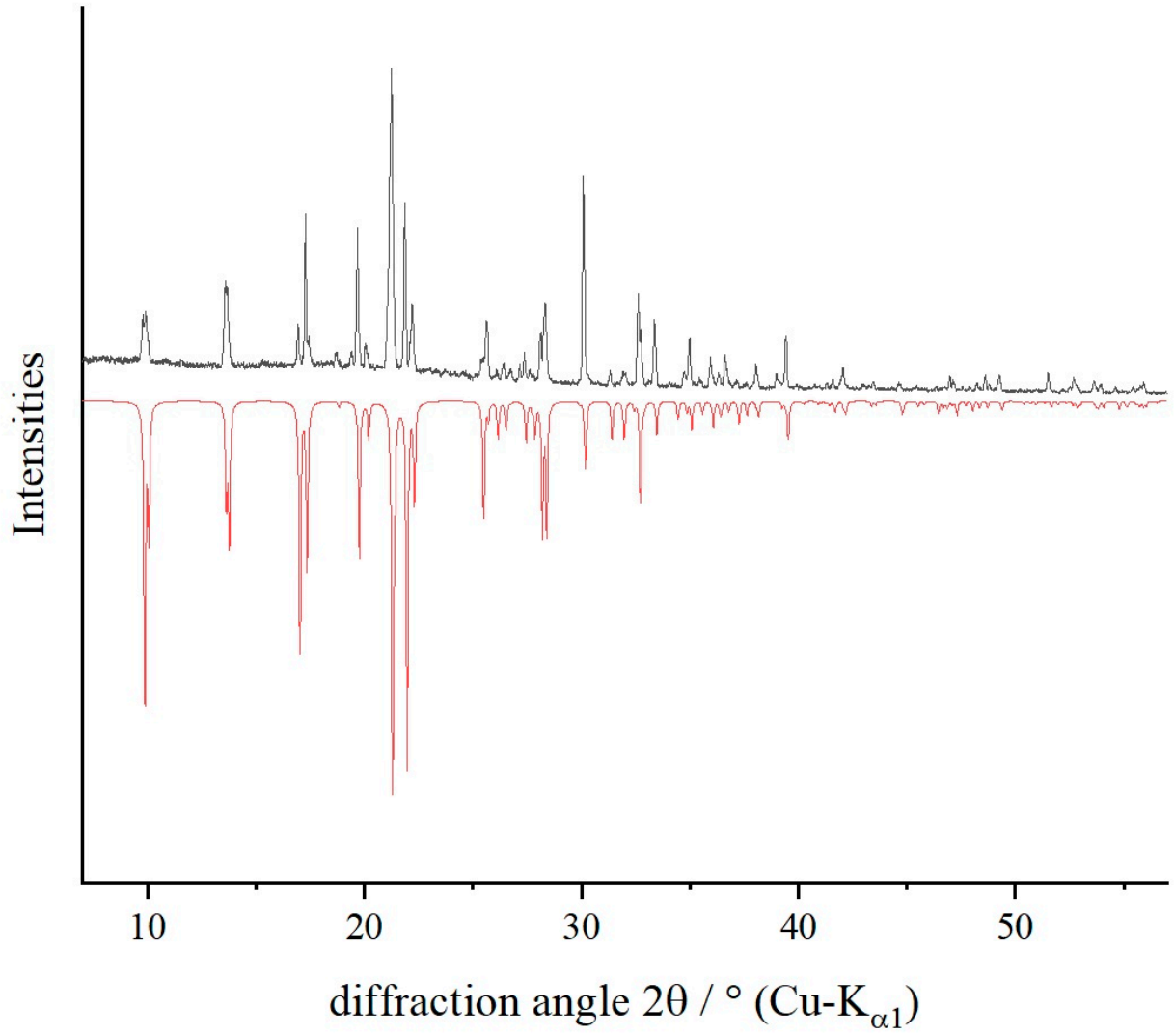

Figure S2. Powder X-ray diffraction pattern of $(N_2H_5)_3[ClO_4][B_{12}H_{12}] \cdot H_2O$ (**II**) (top) and the calculated pattern (bottom).

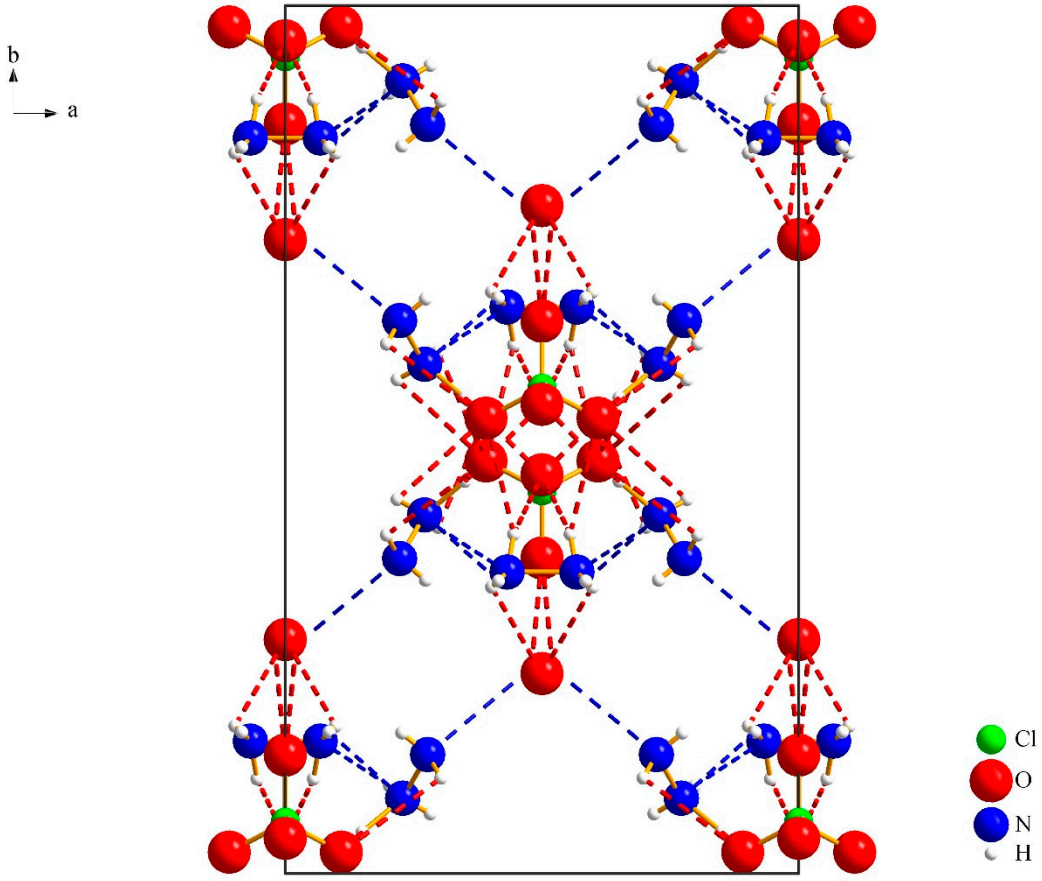

Figure S3. Illustration of the classical hydrogen-bond system in $(N_2H_5)_3[ClO_4][B_{12}H_{12}] \cdot H_2O$ (**II**) with *six* hydrogen atoms for hydrazinium 2.