Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary material

Structural, Theoretical and Spectroscopic Studies of the Dichloride Hexahydrate Cube $[Cl_2(H_2O)_6]^{2-}$

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Table 1S. Values of water occupancy as refined by GSAS, including differences Δ from unity or 1/2 occupation in terms of σ (estimated standard deviation)..

Atom	Refined occupancy	Difference Δ from unity or 1/2 occupancy
O1	1.02(2)	$1\sigma < \Delta < 2\sigma$
H1A	0.44(3)	$2\sigma < \Delta < 3\sigma$
H1B	0.96(2)	$1\sigma < \Delta < 2\sigma$
H1C	0.47(3)	$\Delta < 1\sigma$
O2	1.00(2)	$\Delta < 1\sigma$
H2A	0.95(2)	$1\sigma < \Delta < 2\sigma$
H2B	0.54(3)	$1\sigma < \Delta < 2\sigma$
H2C	0.48(3)	$\Delta < 1\sigma$
O3	1.00(2)	$\Delta < 1\sigma$
H3A	0.54(3)	$1\sigma < \Delta < 2\sigma$
H3B	0.93(2)	$2\sigma < \Delta < 3\sigma$
H3C	0.47(3)	$1\sigma < \Delta < 2\sigma$

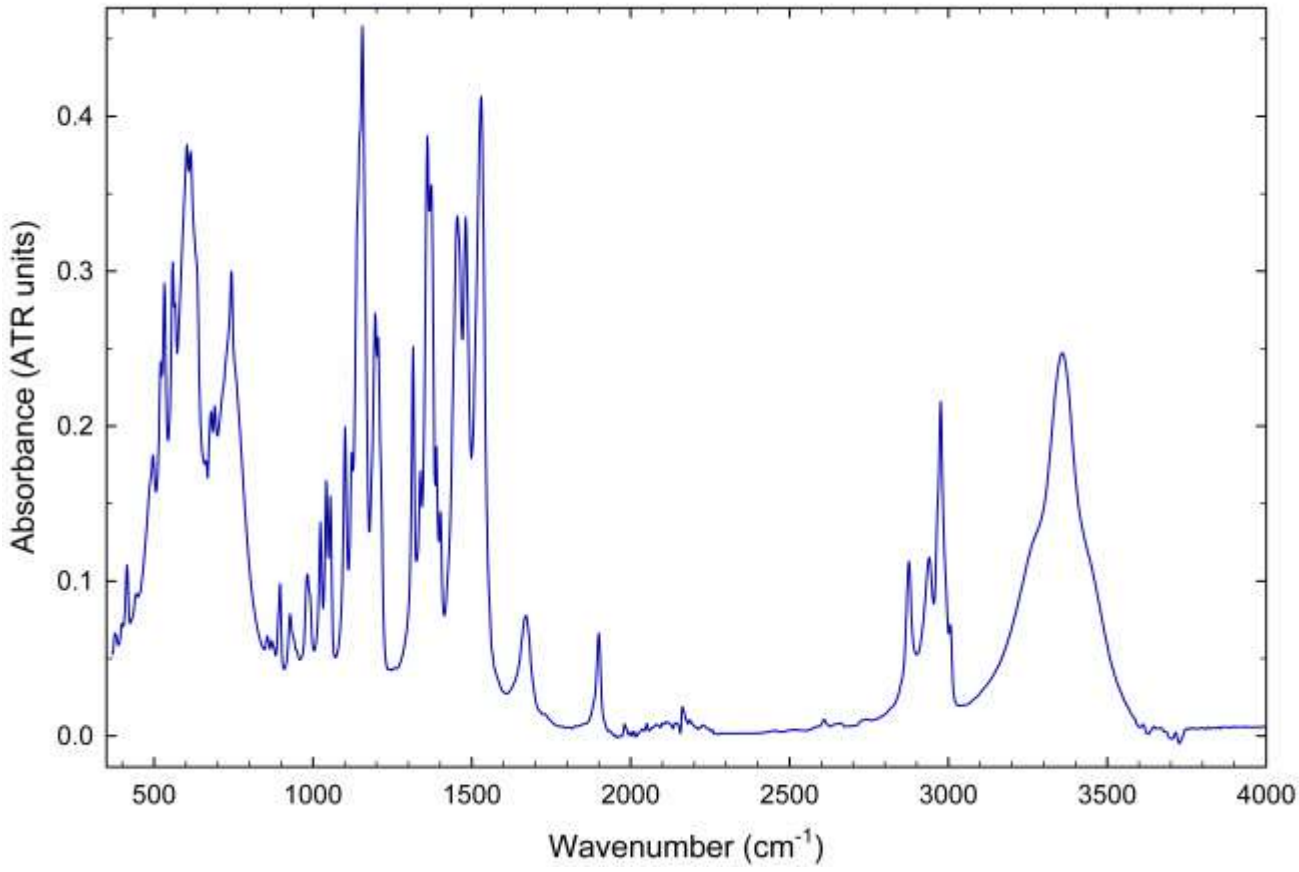


Figure 8S. IR ATR spectrum of $[C_3(N^iPr_2)_3]Cl.3H_2O$.

Comments on neutron structures containing short (< 0.90 Å) O–H bonds for water molecules

Distances are given in the order: O–H, H···O, O···O.

A table of references associated with the CSD codes appears at the end.

ABXNIH: The average of chemically equivalent O–H distances is 0.92 Å.

AMBXPT10 has disordered water molecules.

AMOXNB has one short O–H distance (O14: 0.824 Å, 2.130 Å, 2.947 Å) on a water molecule that is a hydrogen-bond donor to an oxalato ligand and a hydrogen-bond acceptor from another water molecule. Two similar water molecules have longer O–H distances for similar H atoms (O12: 0.951 Å, 1.849 Å, 2.767 Å; and O13: 0.971 Å, 1.825 Å, 2.784 Å). The other H atoms are more weakly H-bonded to an oxalate (O12: 0.941 Å, 2.352 Å, 3.205 Å) or a water molecule (O13: 0.928 Å, 2.293 Å, 3.115 Å; and O14: 0.946 Å, 2.242 Å, 3.146 Å). A consistent trend or obvious explanation for the short O–H distance is not revealed.

AQACMN03: O13 water is H-bond acceptor from another water molecule and an H-bond donor to two acetate ligands (0.839 Å, 2.328 Å, 3.088 Å; and 0.941 Å, 2.131 Å, 2.975 Å); O12, 12a, 12f, and 12g are aqua ligands on Mn^{2+} with H-donors to an acetate ligand (0.850 Å, 1.870 Å, 2.705 Å) and to water (0.981 Å, 1.764 Å, 2.741 Å). No consistent trend.

CBZSUL01: O6 has a short O–H bond at the end of an $[O_3H_7]^+$ chain that is weakly hydrogen bonded to an $–SO_3^-$ group: (0.855 Å, 2.326 Å, 3.155 Å). The other OH on O6 is also a HBD to an $–SO_3^-$ group (0.944 Å, 2.085 Å, 2.950 Å). Three similar OH groups have longer O–H bonds but also shorter H---O hydrogen bonds (O5: 0.944 Å, 1.655 Å, 2.599 Å (other OH is H-bond donor to water (0.975 Å, 1.432 Å, 2.407 Å); O4: 0.936 Å, 1.759 Å, 2.691 Å; 0.959 Å, 1.742 Å, 2.700 Å). The short O–H distance appears to correlate with long O···O and O···H distances.

Table 2S. Hydrogen bonding distances [Å] and angles [°] for water molecules in CBZSUL01.

O atom	O–H	H···O	O···O	O–H···O
O6	0.855	2.326	3.155	163.4
O6	0.944	2.085	2.950	
O5	0.944	1.655	2.599	177.4
O5	0.975	1.432	2.407	178.5
O4	0.936	1.759	2.691	173.0
O4	0.959	1.742	2.700	177.1

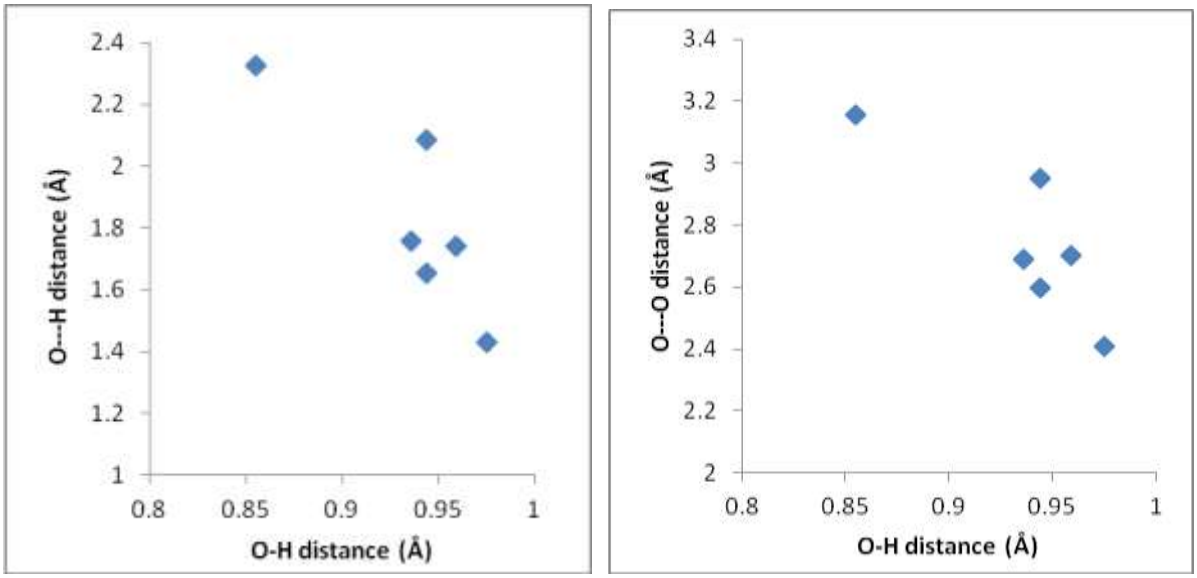
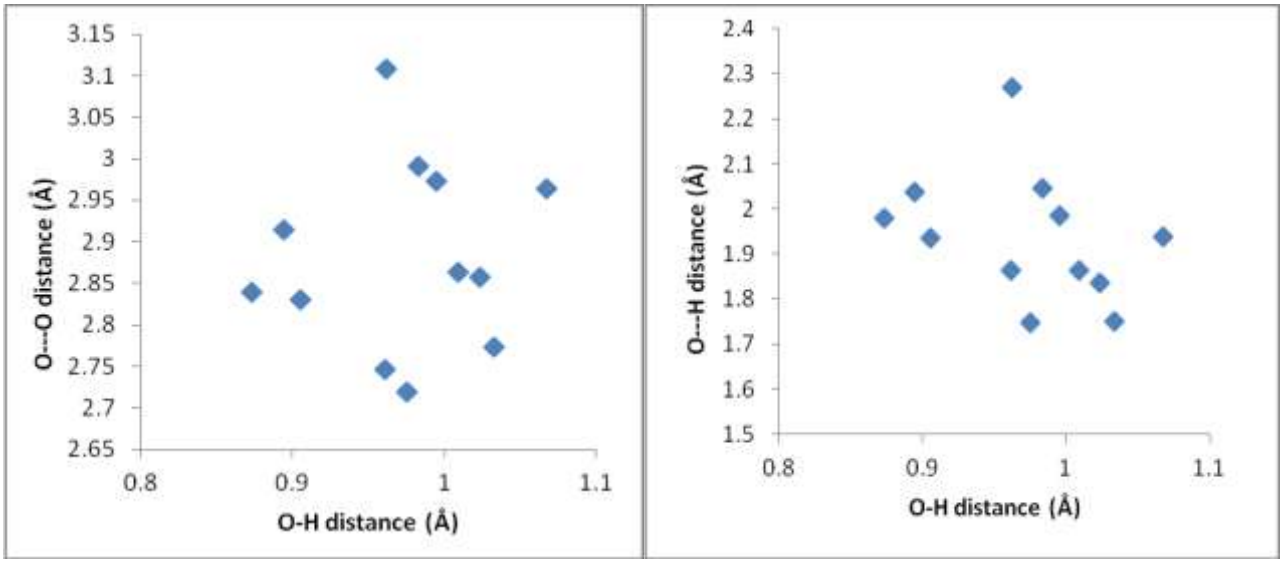


Figure 1S. O-H distances versus (a) H---O and (b) O---O bond lengths for CBZSUL01.

CHXAMH02: O31 acceptor from water and an alcohol, donor to water (1.023 Å) and an alcohol (0.961 Å); O32 acceptor from water and an alcohol, donor to two alcohols (1.033 Å and 0.975 Å); O33 acceptor from an alcohol, donor to an alcohol (0.905 Å) and an ether (1.067 Å); O34 acceptor from two alcohols, donor to an alcohol (0.873 Å) and a water (1.009 Å); O35 acceptor from an alcohol, donor to an alcohol (0.995 Å) and a water (0.894 Å); O36 acceptor from a water, donor to two alcohols (0.983 Å and 0.962 Å). The short O–H bonds don't correlate with short or long O---O or H···O distances, or the HBA species.

Table 3S. Hydrogen bond distances [Å] and angles [°] for water molecules in CHXAMH02.

O atom	O–H	H···O	O···O	O–H···O
O31	1.023	1.835	2.857	176.4
O31	0.961	1.863	2.747	151.6
O32	1.033	1.751	2.773	168.9
O32	0.975	1.748	2.719	174.1
O33	0.905	1.934	2.831	171.0
O33	1.067	1.937	2.964	160.6
O34	0.873	1.979	2.840	
O34	1.009	1.863	2.864	
O35	0.995	1.984	2.973	
O35	0.894	2.038	2.915	
O36	0.983	2.047	2.991	
O36	0.962	2.269	3.108	



(a) (b)

Figure 2S. Plots of (a) O···O versus O–H and (b) O···H versus O–H for CHXAMH02.

CIRVAA01: Has six aqua ligands on a Mg^{2+} centre. All are H-bond donors to a carboxylate. One short O–H distance of 0.858 Å, but the other O–H bonds are similar in nature and the O–H bond distance average is 0.931 Å; and the short O–H bond doesn't correlate to short or long O···O or H···O distances.

CIWKEY01: Has one O–H bond distance of 0.907 Å, however, the three water molecules are all hydrogen bound to a chloride and the average O–H distance is 0.944 Å. O1 is coordinated to Pt^{2+} and is an H-bond donor to two chlorides: O–H = 0.974 Å, H···Cl = 2.163 Å, O···Cl = 3.127 Å; O–H = 0.968 Å, H···Cl = 2.172 Å, O···Cl = 3.139 Å. O2 is H-bond donor to two chlorides: O–H = 0.945 Å, H···Cl = 2.381 Å, O···Cl = 3.325 Å; O–H = 0.907 Å, H···Cl = 2.295 Å, O···Cl = 3.201 Å. Similarly for O3: O–H = 0.939 Å, H···Cl = 2.188 Å, O···Cl = 3.124 Å; O–H = 0.928 Å, H···Cl = 2.265 Å, O···Cl = 3.178 Å.

Table 4S. Hydrogen bond distances [Å] for water molecules in CIWKEY01.

O atom	O–H	H···Cl	O···Cl
O1	0.974	2.163	3.127
O1	0.968	2.172	3.139
O2	0.945	2.381	3.325
O2	0.907	2.295	3.201
O3	0.939	2.188	3.124
O3	0.928	2.265	3.178

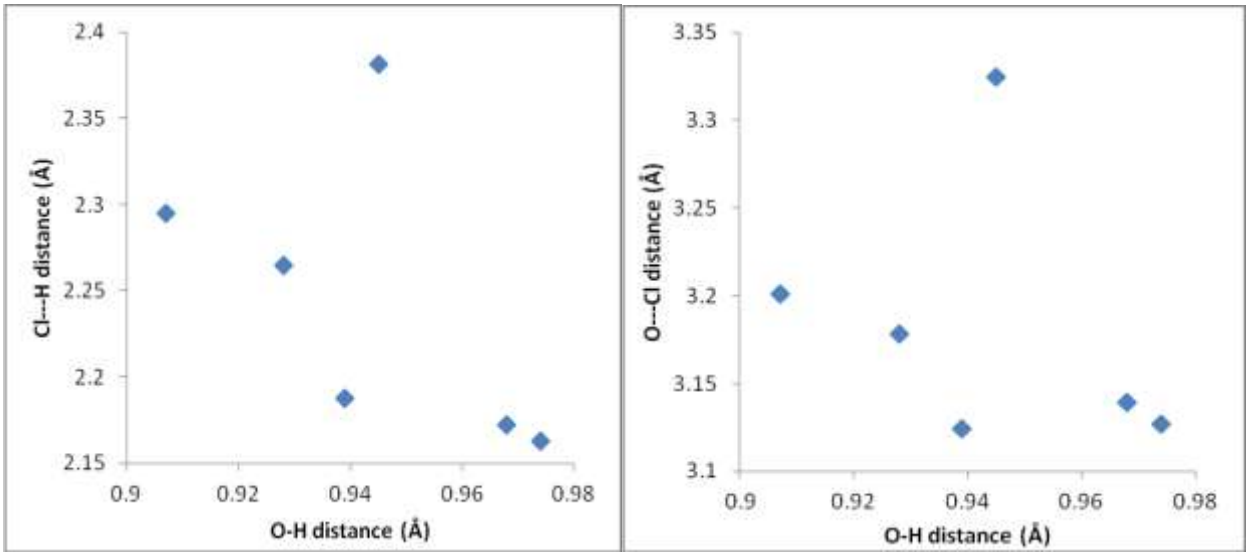


Figure 3S. Plots of (a) H···Cl versus O–H and (b) O···Cl versus O–H for CIWKEY01.

CROXKH02:

O13: 0.842 Å (K···H = 2.901 Å) to oxalato (O···H = 1.905 Å) and 0.766 Å (TWO K–H = 2.763 Å and 2.755 Å) to water (O···H = 2.260 Å);

O14: O–H (0.998 Å) bond donor to K^+ (K–H = 1.208 Å) and oxalate (O–H = 0.953 Å);

O15: Has both O–H perpendicular to a K^+ ion and H-donor to an oxalato ligand (O–H 0.984 Å; O···H 1.891 Å; K–H = 1.706 Å) and a water molecule (O–H 0.767 Å; O···H 1.971 Å; K–H = 1.694 Å).

O16?: Has both O–H perpendicular to a K^+ ion and H-donor to oxalato ligands with O–H = 0.914 Å and 0.908 Å (K–H = 1.405 Å and 1.393 Å);

DADCBL01. This structure has a number of disordered molecules and water molecules with a missing H atom. O19 two proton acceptor and two proton donor interactions: 0.981 Å and 0.934 Å; O20 one proton acceptor and two proton donor interactions (0.944 Å and 0.919 Å); O21 two proton acceptor and two proton donor interactions (1.008 Å and 0.929 Å); O22 one proton acceptor and two proton donor interactions (0.764 Å, 2.081 Å, 2.807 Å and 0.940 Å); O23 missing an H?; O24 one proton acceptor and two proton donor interactions (0.939 Å and 0.959 Å); O25 two proton acceptor and two proton donor interactions: 0.983 Å and 0.967 Å; O26 two proton acceptor and two proton donor interactions: 0.951 Å and 0.900 Å (O···H = 1.968 Å; O···O = 2.833 Å); O27 OH^- group?; O29 two proton donors: 0.872 Å (O···H = 1.833 Å; O···O = 2.704 Å) and 0.899 Å (O···H = 1.819 Å; O···O = 2.718 Å); O30 one proton acceptor and two proton donor interactions 1.035 Å and 0.870 Å (O···H = 1.865 Å; O···O = 2.728 Å); O31 missing an H?.

The average O–H distance is 0.932 Å. One particularly short O–H distance (0.764 Å for O22) appears to be a HBD to an "OH" molecule, so there is probably some unidentified disorder in this region. The other short O–H distances don't have any obvious explanation and are probably due to statistical variation.

Table 5S. Hydrogen bond distances [Å] for water molecules in DADCBL01.

O atom	O–H	H···O	O···O
O19	0.981	1.834	2.802
O19	0.934	2.239	3.070
O20	0.944	2.054	2.931
O20	0.919	2.038	2.950
O21	1.008	1.762	2.758
O21	0.929	1.861	2.784
O22	0.764	2.081	2.807
O22	0.940	1.847	2.765
O24	0.939	1.810	2.737
O24	0.959	1.967	2.889
O25	0.983	1.844	2.804

O25	0.967	1.824	2.766
O26	0.900	1.968	2.833
O29	0.872	1.833	2.704
O29	0.899	1.819	2.718
O30	1.035	1.815	2.827
O30	0.870	1.865	2.728

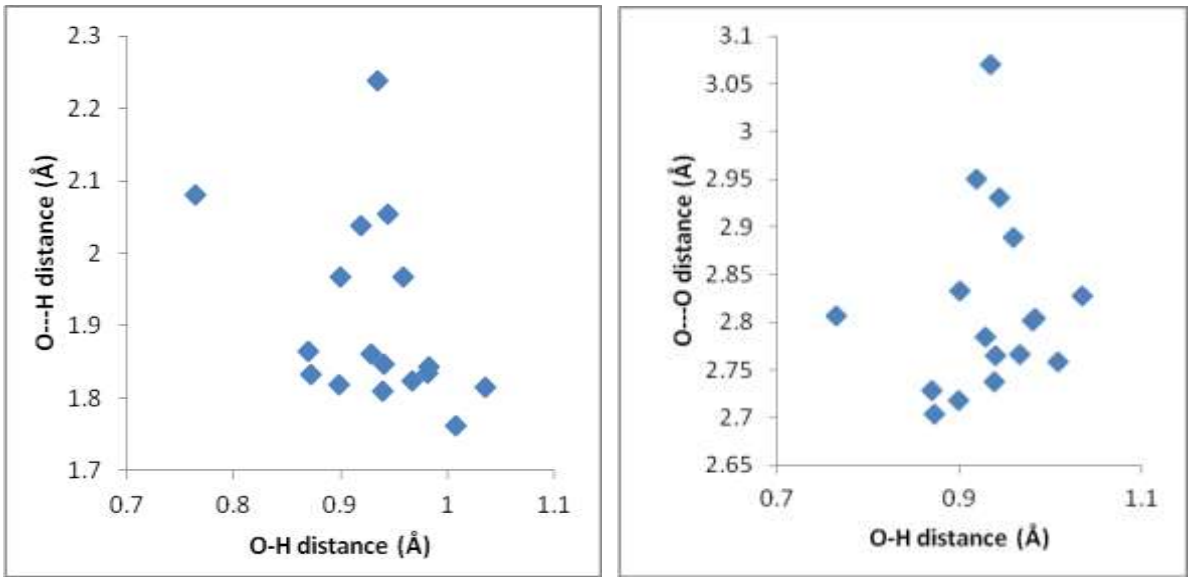


Figure 4S. Plots of (a) H···Cl versus O–H and (b) O···Cl versus O–H for DADCBL01.

DOPBUF01 O4/O4d coordinated to Mn^{2+} and is a proton donor to water and coordinated ketone, 0.937 Å and 0.966 Å; O5 coordinated to Cu^{2+} and is a proton donor to a coordinated ketone, 0.930 Å; O6 proton acceptor from water, proton donor to coordinated ketones, 0.927 Å (O···H = 2.046 Å; O···O = 2.948 Å) and 0.909 Å (O···H = 1.930 Å; O···O = 2.768 Å).

EPHEDH03. Powder diffraction data

FAYQOM02 has one O–H distance at 0.868 Å, but data collected at a lower temperature gave no distances shorter than 0.926 Å.

HBPCUS01: O7 coordinated to Cu^{2+}, donor to water (0.899 Å, 1.716 Å, 2.615 Å) and sulfate (0.865 Å, 1.753 Å, 2.610 Å); O8 acceptor from two water, donor to two water 1.012 Å and 1.005 Å; O9 acceptor from one water, donor to mu-OH (1.197 Å) and sulphate (0.942 Å); O10 acceptor from water and aromatic CH, donor to mu-OH (1.135 Å) and water (0.895 Å, 1.991 Å, 2.879 Å); O11 acceptor from one water, donor to water (0.963 Å) and sulfate (0.760 Å, 1.884 Å, 2.640 Å).

HBPCUS01 has two short O–H bond distances (0.899 Å and 0.865 Å) associated with a water molecule coordinated to a Cu^{2+} centre as well as a short distance (0.760 Å) for a water molecule acting as an HBD to a sulfate ion. There appears to be some correlation of short O–H bond distances with long O···H distances.

Table 6S. Hydrogen bond distances [Å] for water molecules in HBPCUS01.

O atom	O–H	H···O	O···O
O7	0.899	1.716	2.615
O7	0.865	1.753	2.610
O8	1.012	1.790	2.802
O8	1.005	1.655	2.660
O9	1.197	1.553	2.740
O9	0.942	1.800	2.711
O10	1.135	1.696	2.814
O10	0.895	1.991	2.879
O11	0.963	1.881	2.828
O11	0.760	1.884	2.640

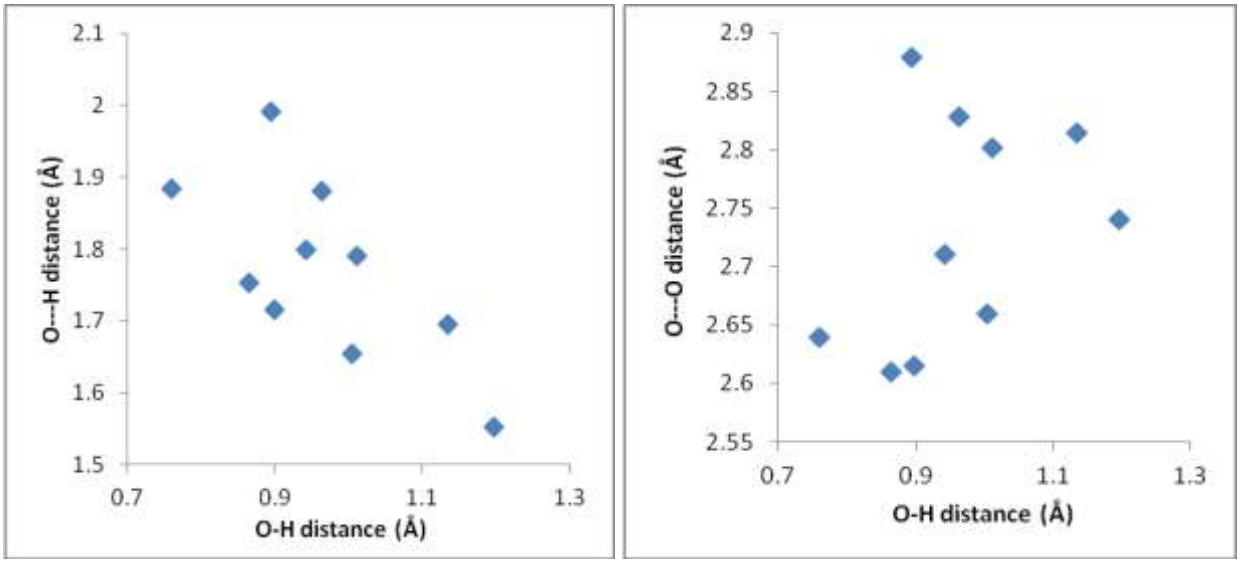


Figure 5S. Plots of (a) H---Cl versus O–H and (b) O---Cl versus O–H for HBPCUS01.

LIHPAL03 has one O–H distance of 0.882 Å for data collected at 295 K, however, data collected at 100 K and 15 K gave no O–H distances less than 0.927 Å.

LIPWEM02 uses powder diffraction data and has large errors.

MNFORD01 has large errors O–H = 0.89(3) Å. Two waters coordinated to Mn, each a proton donor to two formato ligands, O2 0.987 Å (O···H = 1.770 Å, O···O = 2.710 Å) and 0.978 Å (O···H = 1.783 Å, O···O = 2.760 Å); O4 0.948 Å (O···H = 1.858 Å, O···O = 2.800 Å) and 0.879 Å (O···H = 1.831 Å, O···O = 2.709 Å).

NACTMO02 has five water molecules with one distance at 0.89(1) Å. O9 bridges two Na^+ ions, proton donor to one water (0.964 Å) and one carboxylato ketone O (0.939 Å); O10 coordinated to one Na^+ and proton acceptor from one water, proton donor to terminal oxo ligand on Mo (0.949 Å, 1.826 Å, 2.772 Å) and carboxylato ketone O (0.983 Å); O11 bridges two Na^+ ions and H-bond donor to mu-oxo (0.929 Å, 2.153 Å, 3.007 Å) and ketone O of a carboxylato (0.951 Å); O12 coordinated to Na^+ H-bond donor to thiolato (0.974 Å, S···H = 2.330 Å, O···S = 3.252 Å) and ketone O of a carboxylato (0.946 Å); O13 coordinated to Na^+, proton donor to mu-oxo (0.940 Å, 2.048 Å, 2.976 Å) and a terminal oxo ligand on Mo (0.887 Å, 2.237 Å, 3.119 Å).

NACTMO02 displays one short O–H bond distance (0.887 Å) for a water molecule coordinated to a Na^+ ion with a long donor interaction to a terminal oxo ligand (O···O = 3.119 Å). Four similar water molecules (all coordinated to at least one Na^+ ion) display longer O–H distances (0.929–0.983 Å) but have shorter HBD interactions (O···O = 2.722–3.007 Å).

Table 7S. Hydrogen bond distances [Å] for water molecules in NACTMO02.

O atom	O–H	H···O	O···O
O9	0.964	1.800	2.755
O9	0.939	1.970	2.896
O10	0.949	1.826	2.772
O10	0.983	1.739	2.722
O11	0.929	2.153	3.007
O11	0.951	1.967	2.901
O12	0.946	1.818	2.752
O13	0.940	2.048	2.976
O13	0.887	2.237	3.119

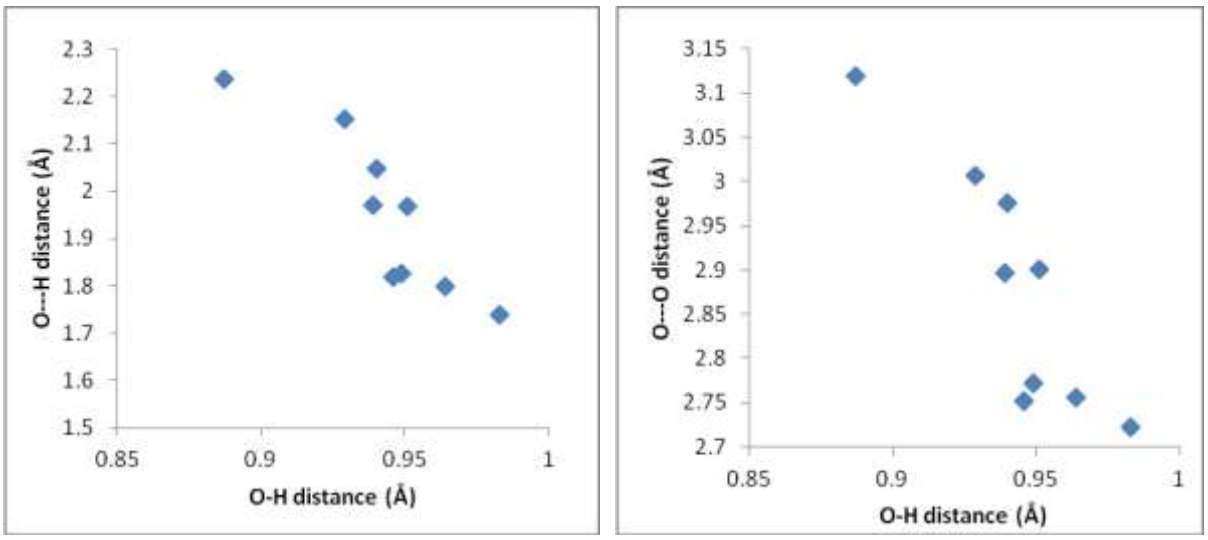


Figure 6S. Plots of (a) H···Cl versus O–H and (b) O···Cl versus O–H for NACTMO02.

NSMEDT02 has disordered water molecules with large errors.

PIBZIK01: O1 is coordinated to Ni and is an H-bond donor to a nitrate (0.880 Å, 1.794 Å, 2.672 Å) and a water molecule that is only half occupied (0.832 Å, 1.896 Å, 2.678 Å); O5/O5b each have half occupancy and are related by symmetry. They are proton acceptors from one water and a proton donor to two nitrates (0.958 Å and 0.958 Å). R-factor = 16%. Considering the disorder and high R-factor, the data is probably not reliable.

QOYHUH: two water molecules, each is a proton acceptor from an alcohol and a proton donor to two ether oxygen atoms: 0.897 Å, 2.148 Å, 2.993 Å; 1.026 Å, 2.027 Å, 3.042 Å; 0.904 Å, 1.973 Å, 2.865 Å; 1.017 Å, 2.135 Å, 3.148 Å. No obvious trend for four similar environments. Within the range of normal variation.

Table 8S. Hydrogen bond distances [Å] for water molecules in QOYHUH.

O atom	O–H	H···O	O···O
O	0.897	2.148	2.993
O	1.026	2.027	3.042
O	0.904	1.973	2.865
O	1.017	2.135	3.148

SIKJUR: O2 is coordinated to a Ba^{2+} ion and has weak interactions with two cyano ligand N atoms (symmetry-related O–H bonds) O–H = 0.907 Å, N···H = 2.610 Å, O···N = 3.443 Å; O3 and O4 are disordered over two positions.

ZOZVUF contains a water molecule that is a hydrogen-bond acceptor from ROH and RNH_2 groups and a hydrogen-bond donor to two ROH groups. The two H_w···O distances (2.04(4) Å and 2.08(4) Å) are longer than in our cluster (average = 1.918 Å) while the O–H_w bonds are shorter (0.83(4) Å and 0.77(4) Å versus 0.900 Å). The O···O distances are similar (2.832(4) Å and 2.809(4) Å versus 2.811 Å). The errors are quite large.

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