Electronic Supplementary Information for Dalton Transactions

Supplementary Data

to

Alkali Metal-Sulfur Dioxide Complexes Stabilized by Halogenated *closo*-Dodecaborate Anions

Janis Derendorf,[a] Mathias Keßler,[a] Carsten Knapp,[*a] Monika Rühle,[a] Christoph Schulz[a]

[a] *Institut für Anorganische und Analytische Chemie, Albert-Ludwigs Universität Freiburg, Albertstr. 21, 79104 Freiburg i. Br., Germany. E-mail: carsten.knapp@ac.uni-freiburg.de; Fax: +49-761-203-6001; Tel: +49-761-203-6150.*

1. Quantumchemical calculations

Table S1 Calculated (PBE0/def2-TZVPP) total energies and zero point energies (ZPE) for $M(OSO)^+$ (M = Li, Na, K, Rb, Cs)

Compound	Total energy (a.u.)	ZPE (a.u.)	Total energy including ZPE (a.u.)
Li^+	-7.262402	-	-7.262402
$[Li(OSO)]^+$	-555.719199	0.008874	-555.710324
Na^+	-161.981343	-	-161.981343
$[Na(OSO)]^+$	-710.423337	0.008162	-710.415175
K^+	-599.578330	-	-599.578330
$[K(OSO)]^+$	-1148.011081	0.007927	-1148.003154
Rb^+	-23.927293	-	-23.927293
$[Rb(OSO)]^+$	-572.357386	0.007792	-572.349594
Cs^+	-19.996641	-	-19.996641
$[Cs(OSO)]^+$	-568.424466	0.007735	-568.416731
SO_2	-548.411377	0.007222	-548.404155

2. IR spectra of $[Oct_3NH]_2[B_{12}X_{12}]$ (X = F - I) salts in the solid state

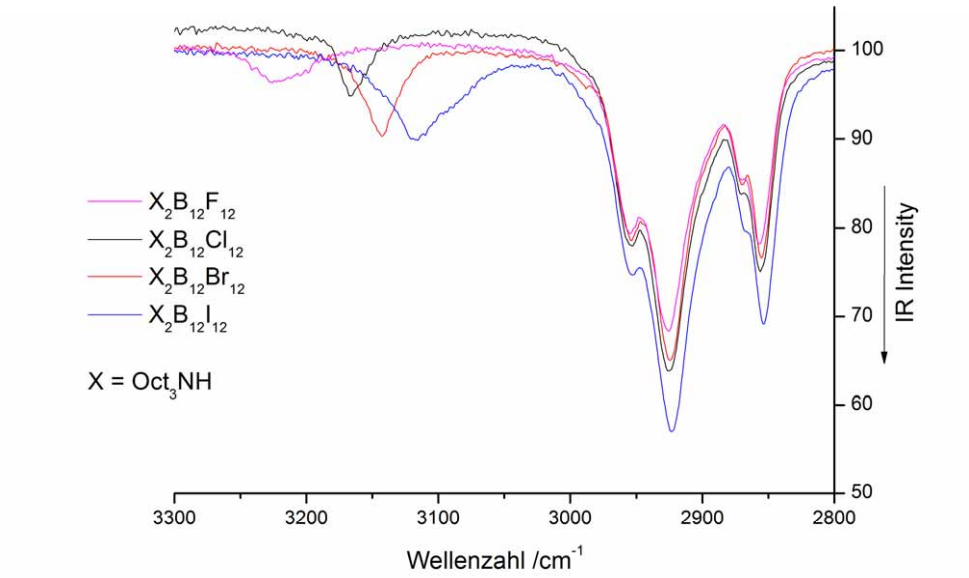

Fig. S1. IR spectra of $[Oct_3NH]_2[B_{12}X_{12}]$ (X = F - I) salts in the solid state

3. Structure figures

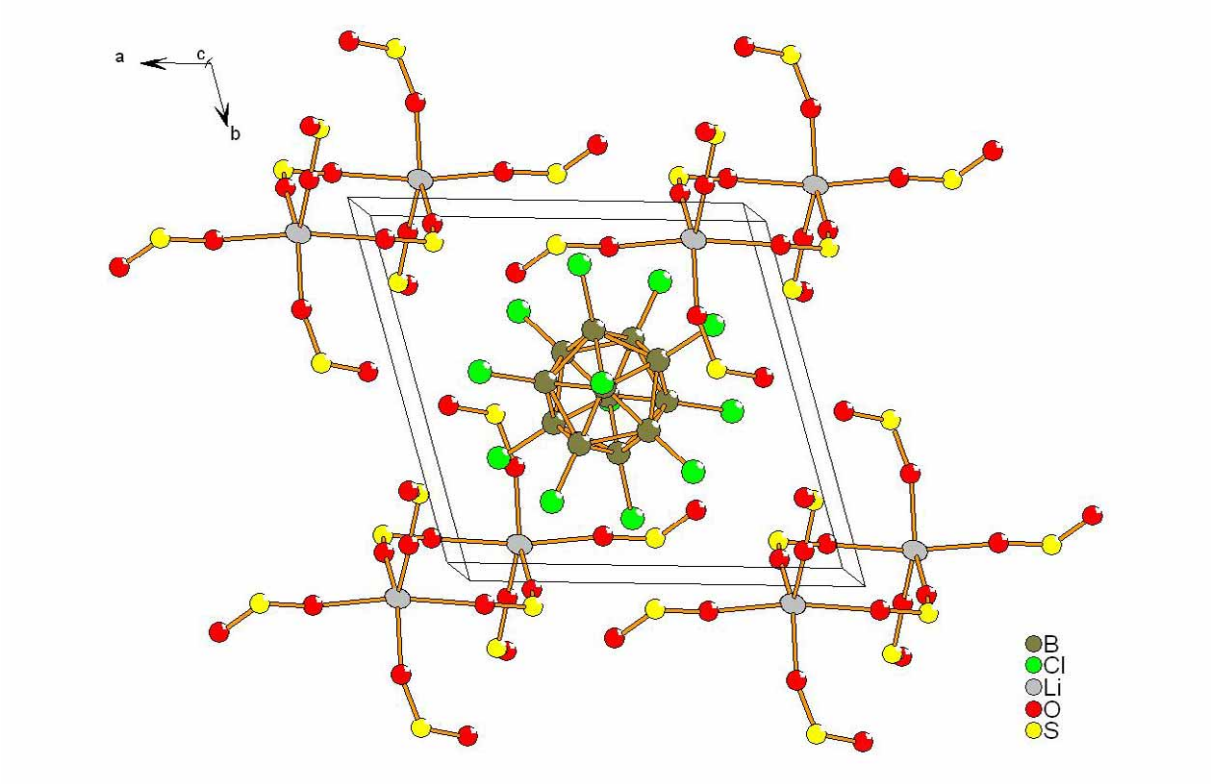

Fig. S2. Unit cell of $[Li_2(SO_2)_8][B_{12}Cl_{12}]$

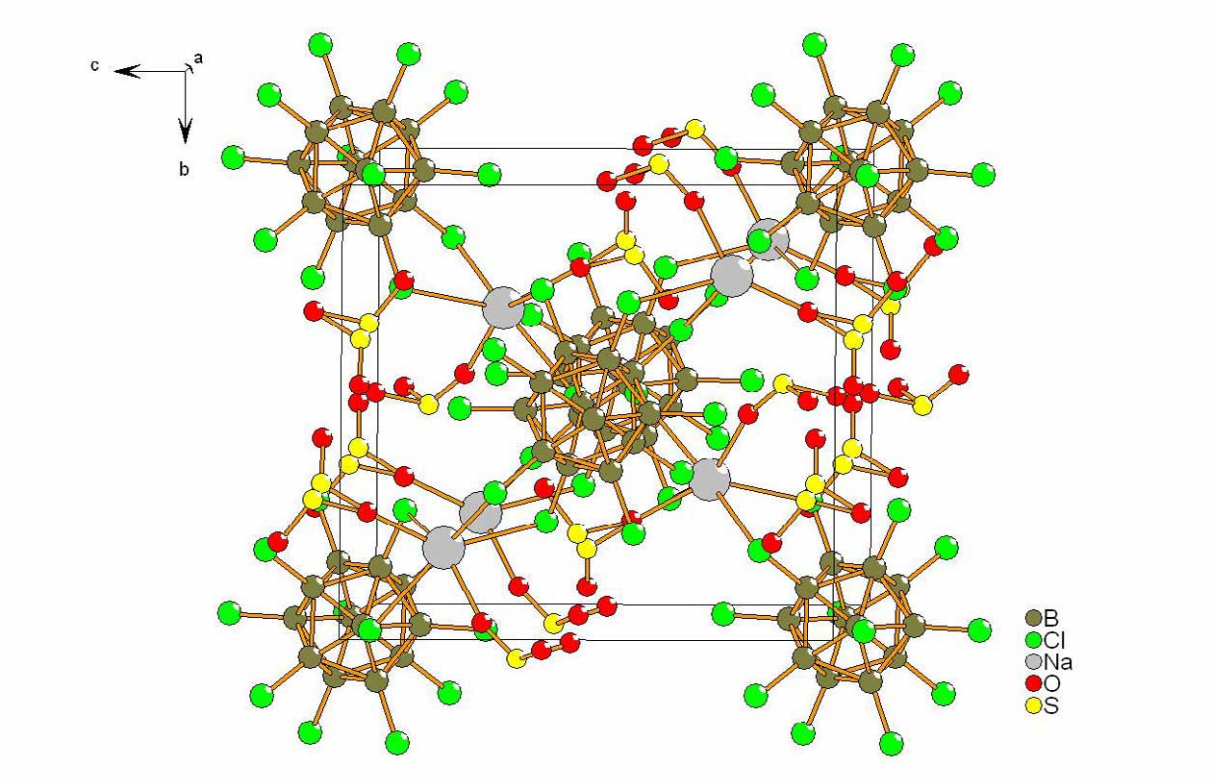

Fig. S3. Unit cell of $Na_2[B_{12}Cl_{12}]\cdot 4SO_2$

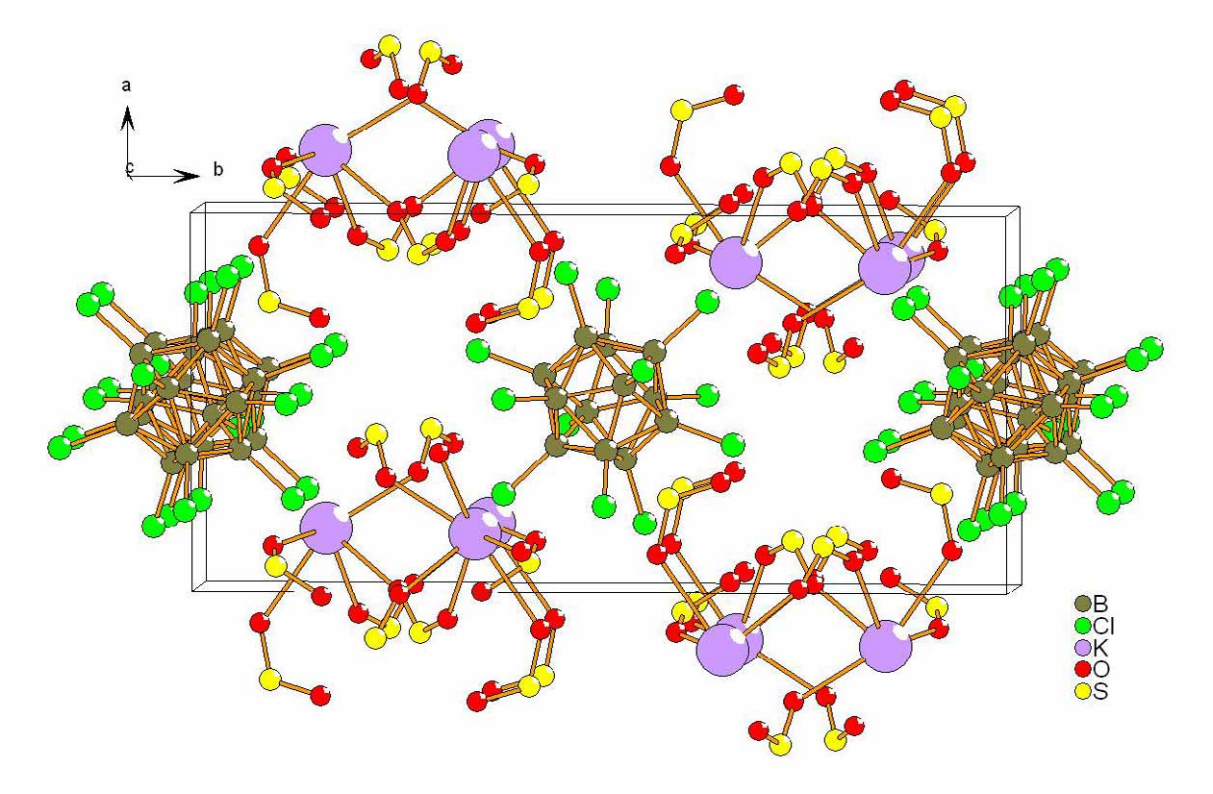

Fig. S4. Unit cell of $K_2[B_{12}Cl_{12}]\cdot 8SO_2$

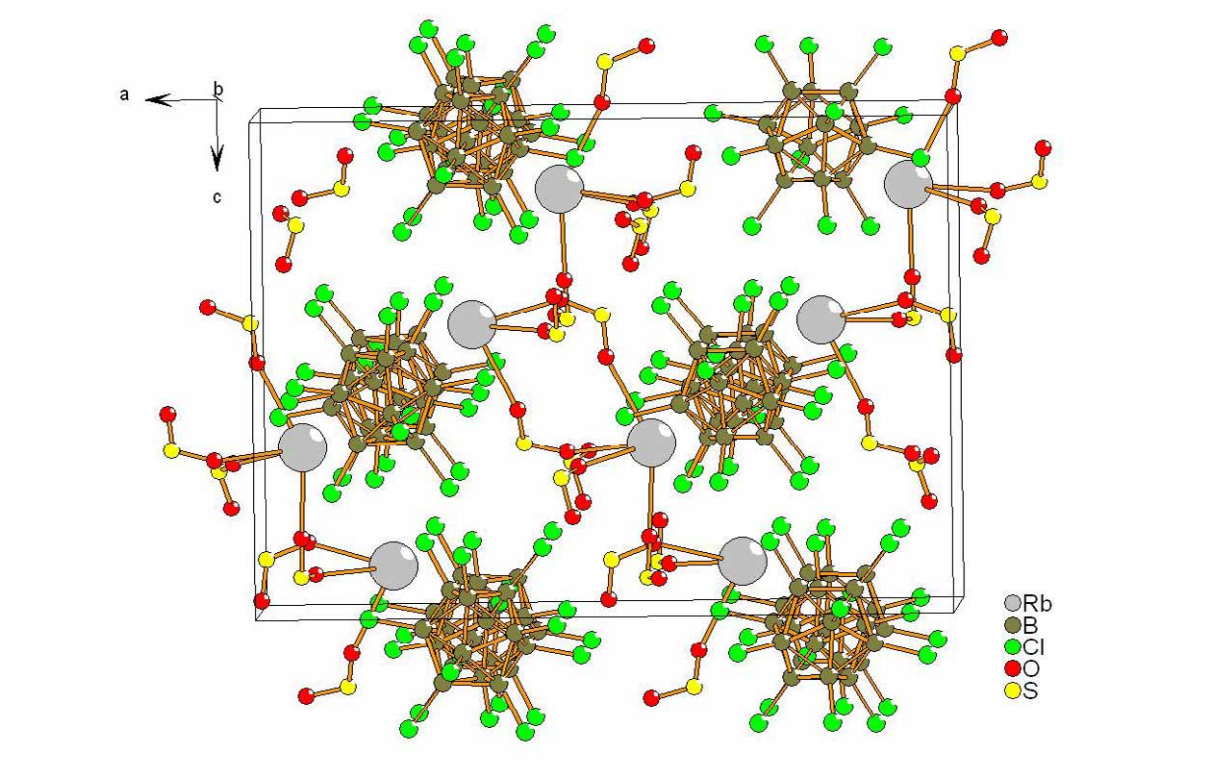

Fig. S5. Unit cell of $Rb_2[B_{12}Cl_{12}]\cdot 4SO_2$

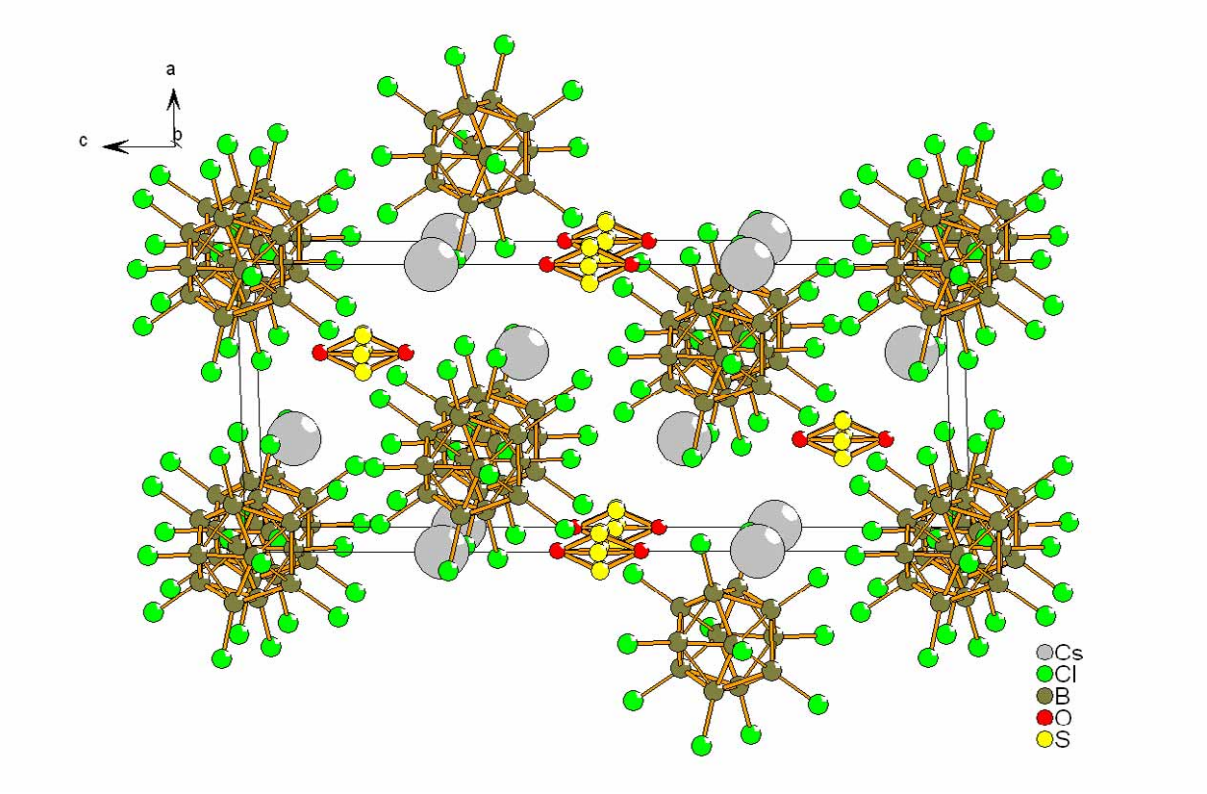

Fig. S6. Unit cell of $Cs_2[B_{12}Cl_{12}]\cdot SO_2$

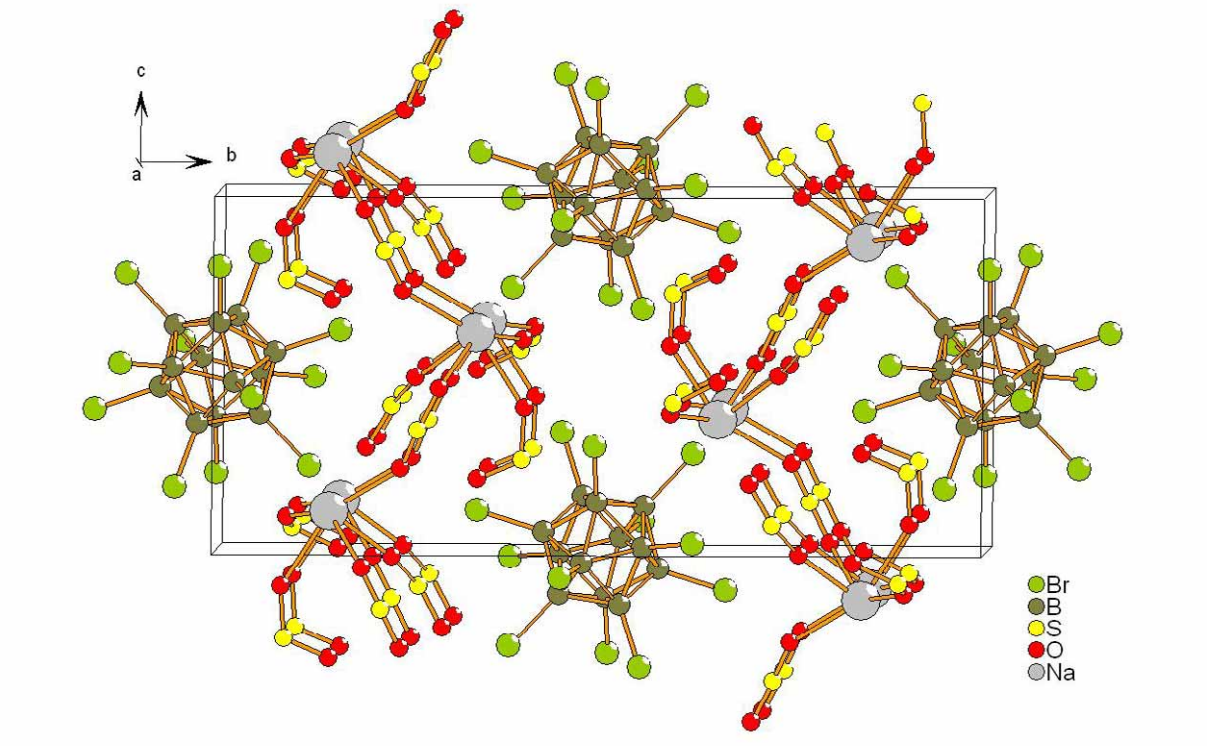

Fig. S7. Unit cell of $Na_2[B_{12}Br_{12}]\cdot 8SO_2$

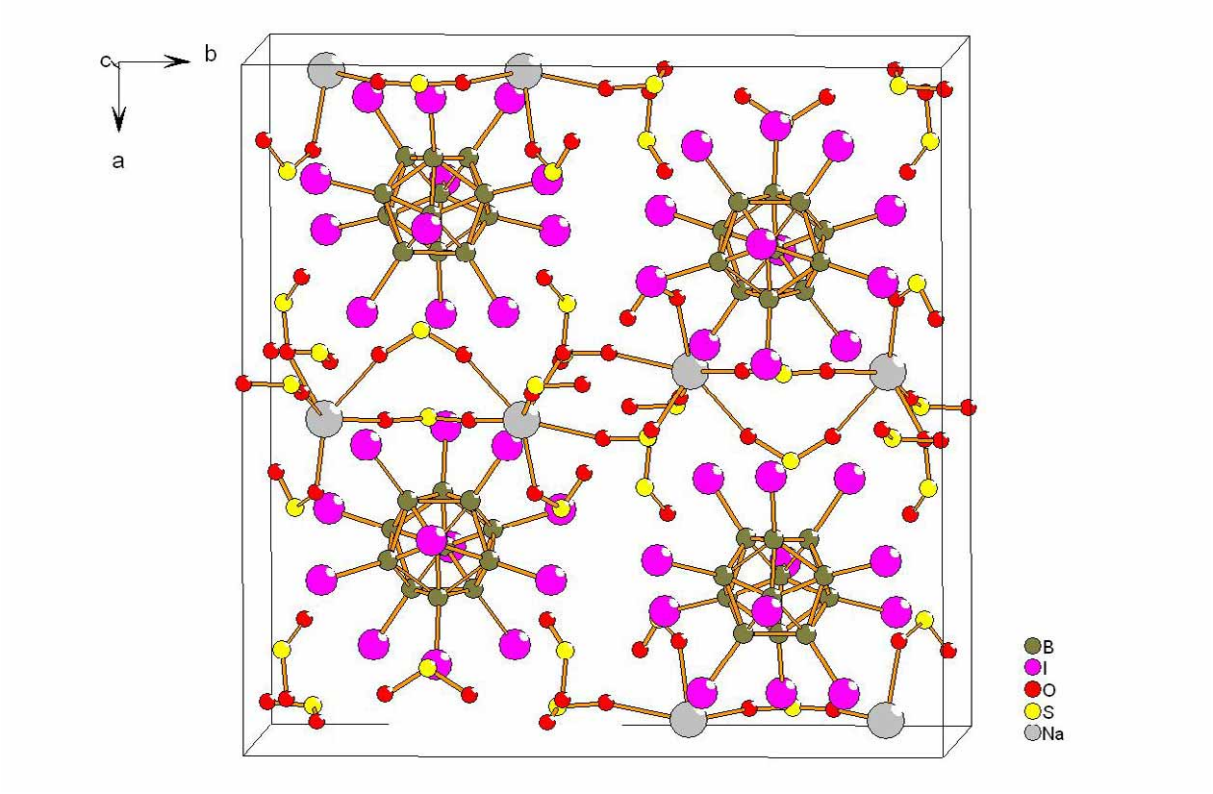

Fig. S8. Unit cell of $Na_2[B_{12}I_{12}]\cdot 8SO_2$

4. Structure of $Na_2[B_{12}H_{12}]\cdot 6SO_2\cdot 2H_2O$ and $Na_2[B_{12}I_{12}]\cdot 8SO_2\cdot H_2O$

The parent compound $Na_2[B_{12}H_{12}]$ cannot be dried with $SOCl_2$ in order to avoid chlorination of the boron cluster. Therefore $Na_2[B_{12}H_{12}]\cdot 6SO_2\cdot 2H_2O$ has crystallized with two molecules of water (Fig. S9). Figure S10 shows the crystal structure of $Na_2[B_{12}I_{12}]\cdot 8SO_2\cdot H_2O$ containing one water molecule. The influence of the coordinated water molecule on the overall structure in this case is small as can be seen from comparison of the structures of $Na_2[B_{12}I_{12}]\cdot 8SO_2$ (Fig. 8, main text) and $Na_2[B_{12}I_{12}]\cdot 8SO_2\cdot H_2O$ (Fig. S10). Both structures contain similar chains of Na^+ bridged by SO_2 molecules. The larger $[B_{12}I_{12}]^{2-}$ anion is able to bridge two Na^+ cations and coordinates to both cations in a η^2 fashion. The small parent anion $[B_{12}H_{12}]^{2-}$ is significantly different from the halogenated anions. It does not form any contacts to the Na^+ cation. The Na^+ cations in $Na_2[B_{12}H_{12}]\cdot 6SO_2\cdot 2H_2O$ are connected by bridging SO_2 and H_2O molecules to give a three-dimension network. Water is a much stronger donor than SO_2 as evident from the Na-O distances ($Na_2[B_{12}H_{12}]\cdot 6SO_2\cdot 2H_2O$: av. Na-OSO 252 pm, Na-$OH_2$ 236 pm; $Na_2[B_{12}I_{12}]\cdot 8SO_2\cdot H_2O$: av. Na-OSO 246 pm, Na-$OH_2$ 221 pm).

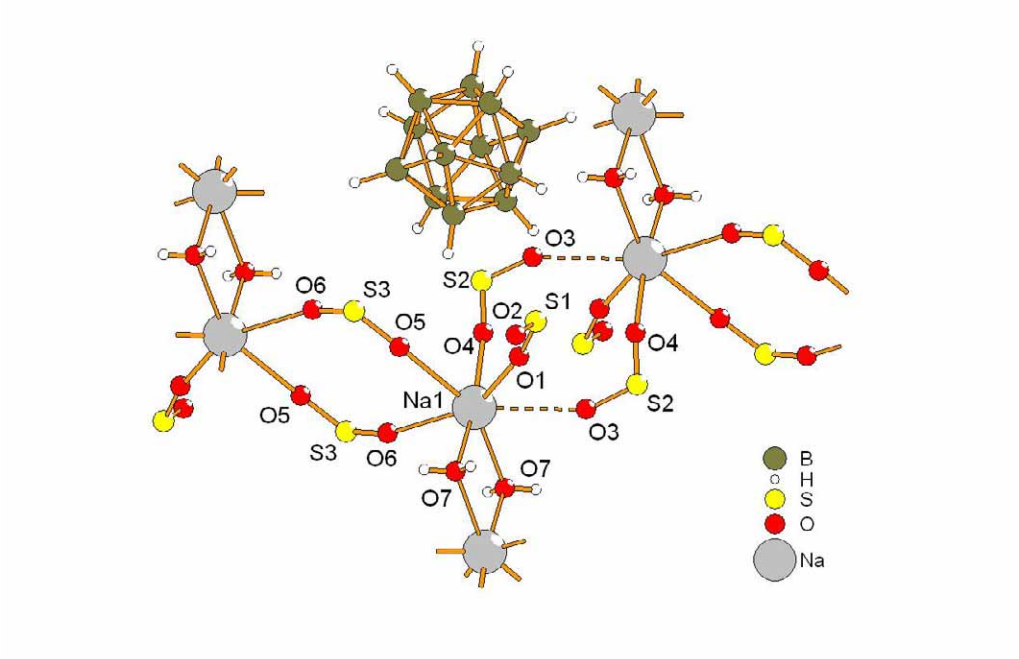

Fig. S9. Section of the crystal structure of $Na_2[B_{12}H_{12}]\cdot 6SO_2\cdot 2H_2O$. Selected distances [pm] and angles [°]: Na1-O1 242.25(15), Na1-O3 274.5(2), Na1-O4 234.50(15), Na1-O5 251.35(15), Na1-O6 262.10(17), Na1-O7 236.43(15), O-S 140.96(13)-142.18(13), O-S-O 116.72(9)-117.98(8).

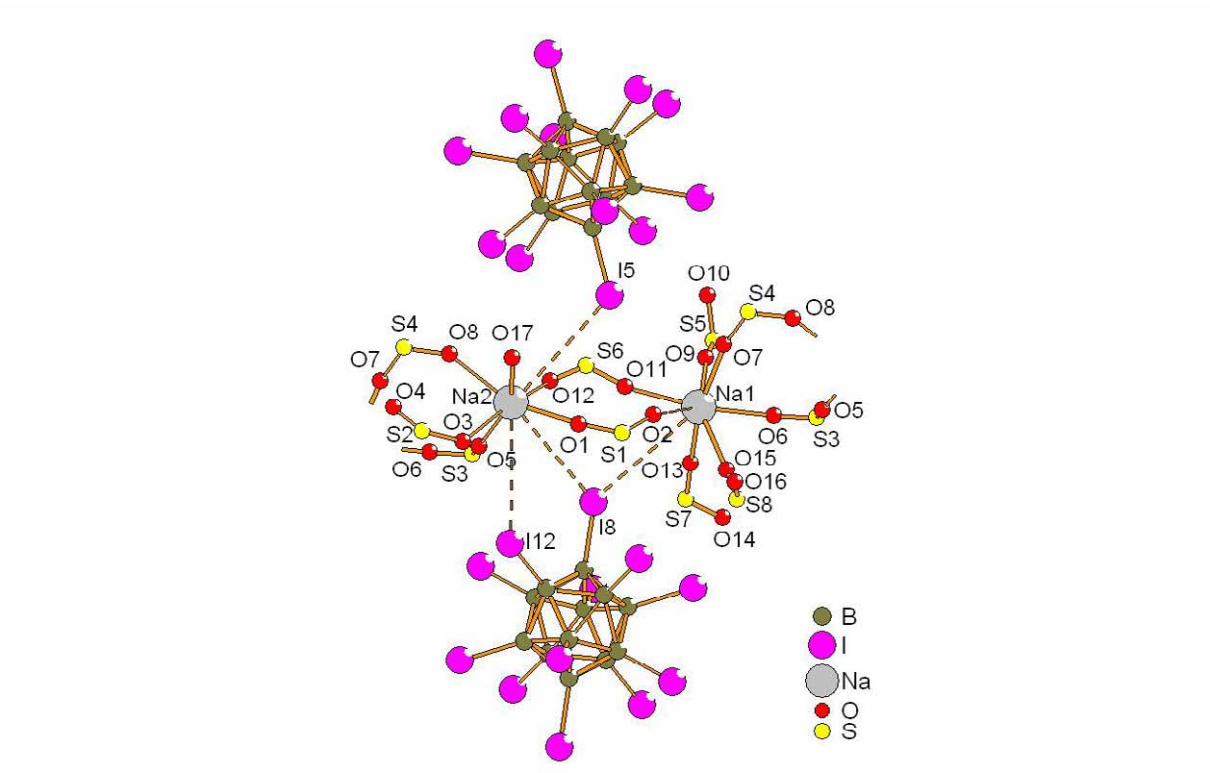

Fig. S10. Section of the crystal structure of $Na_2[B_{12}I_{12}]\cdot 8SO_2\cdot H_2O$. The hydrogen atoms belonging to the water molecule were not found from the electron density map. Selected

distances [pm] and angles [°]: Na1-O2 284.1(13), Na1-O6 240.7(11), Na1-O7 235.6(10), Na1-O9 252.9(11), Na1-O11 237.5(11), Na1-O13 236.9(11), Na1-O15 251.8(11), Na2-O1 232.6(14), Na2-O3 232.6(149, Na2-O5 231.9(13), Na2-O8 259.1(14), Na1-O12 252.2(12), Na1-O17 221.2(14), Na1-I8 437.8(6), Na2-I5 451.6(7), Na2-I7 435.3(7), Na2-I12 445.5(8), O-S 138.6(11)-144.7(10), O-S-O 116.0(7)-119.7(7).

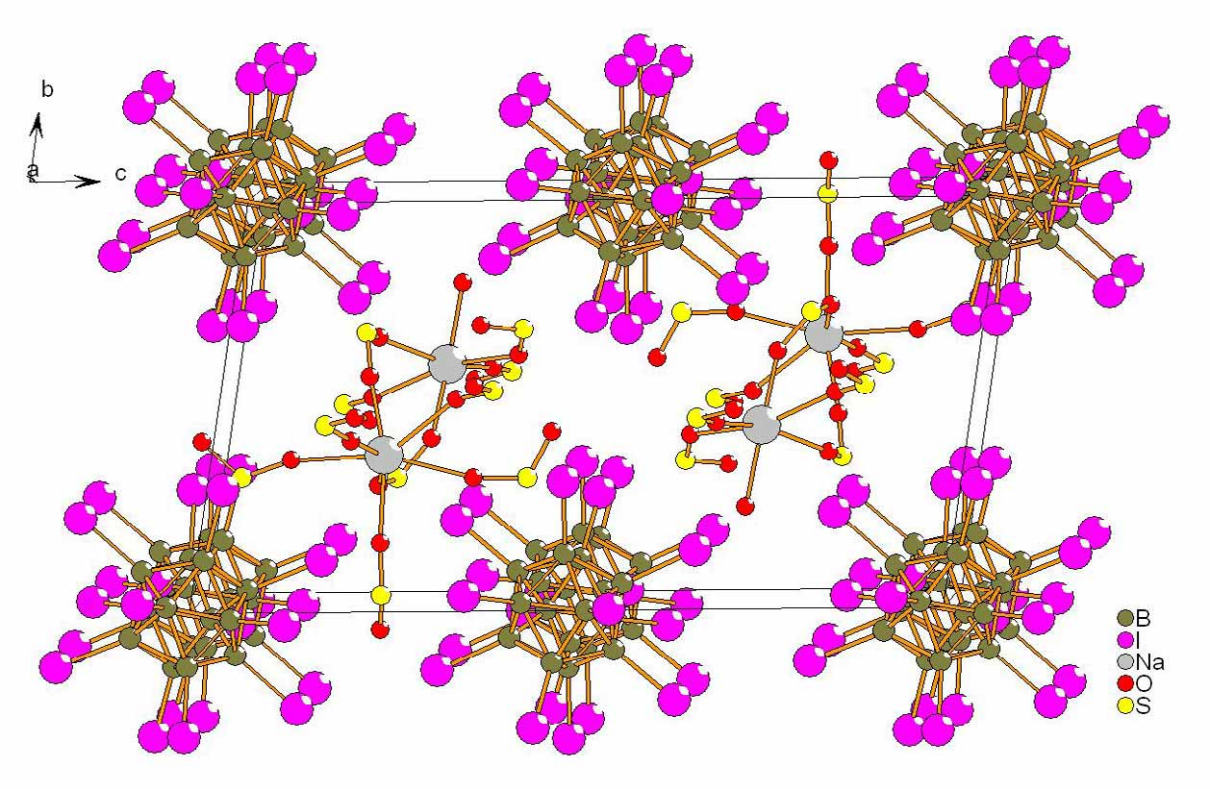

Fig. S11. Unit cell of $Na_2[B_{12}I_{12}]\cdot 8SO_2\cdot H_2O$

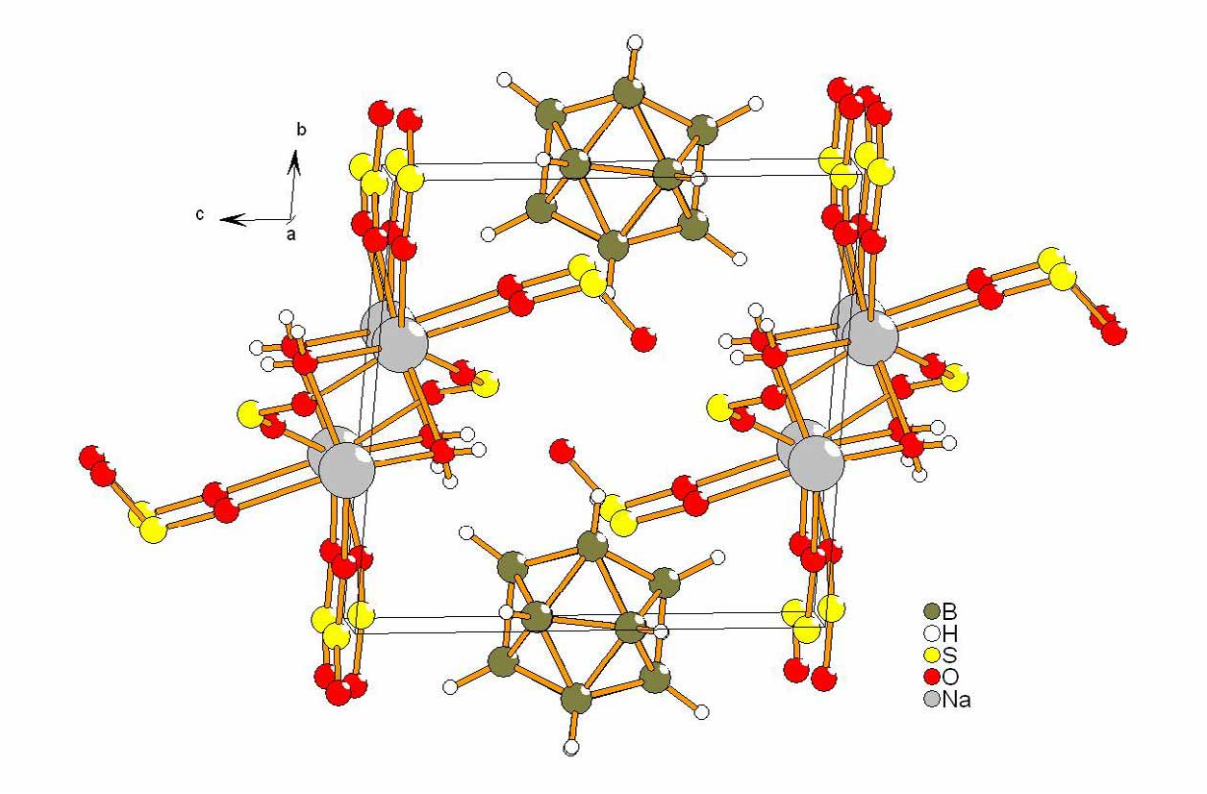

Fig. S12. Unit cell of $Na_2[B_{12}H_{12}]\cdot 6SO_2\cdot 2H_2O$