

Supplementary Information

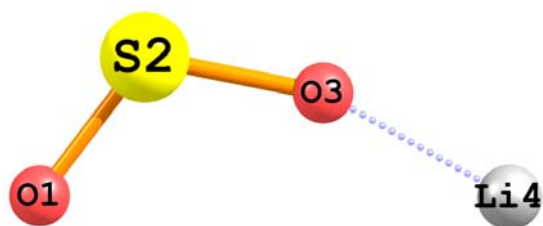
to

**How to overcome Coulomb explosions in labile dications by using
the $[\text{B}_{12}\text{Cl}_{12}]^{2-}$ dianion**

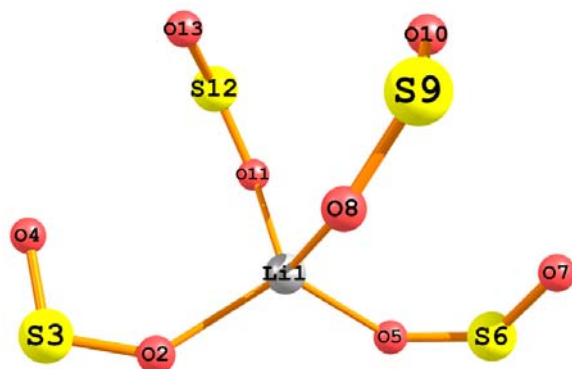
Carsten Knapp, Christoph Schulz*

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

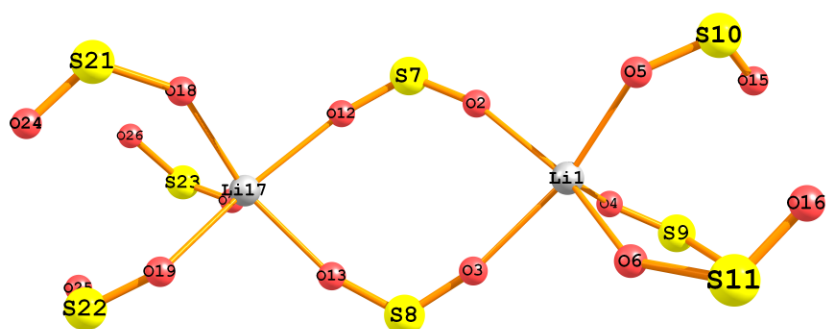
S1. Calculated structures (MP2/def2-TZVPP)



8	1.816752100	-0.388562900	0.000000000
16	0.871798900	0.692601200	0.000000000
8	-0.554673100	0.336268400	0.000000000
3	-2.133878000	-0.640306700	0.000000000



3	-0.793854800	0.005822000	0.038810200
8	-1.777719000	1.656359500	0.503122600
16	-1.646987800	3.093470500	0.272190500
8	-0.521296100	3.542227200	-0.512706300
8	-1.842776100	-1.629073700	-0.330779700
16	-1.709789600	-3.068420400	-0.115656600
8	-0.519036500	-3.534405600	0.554887800
8	0.434552400	-0.461203300	1.532363800
16	1.728527600	-1.128973800	1.665658000
8	2.402364000	-1.519745200	0.450644400
8	0.296549500	0.451655500	-1.563870300
16	1.580940000	1.101903200	-1.819994000
8	2.368526500	1.490384000	-0.674670400



3	2.763279200	-0.527781700	0.065164200
8	1.578128100	1.238052100	-0.347361100
8	0.871400200	-1.667359100	-0.410179100
8	3.608559300	-0.857377200	-1.718384700
8	4.111086000	0.728144300	0.964003800
8	3.225500500	-2.163640300	1.199215900
16	0.481071800	2.149460000	-0.619836100
16	-0.481071800	-2.149460000	-0.619836100
16	4.762407600	-1.614476500	-2.208798800
16	5.534911000	1.044109900	0.844857600
16	4.393094900	-2.752224600	1.857640300
8	-0.871400200	1.667359100	-0.410179100
8	-1.578128100	-1.238052100	-0.347361100
8	5.367771600	-2.556156300	-1.298158800
8	6.245434200	0.474039000	-0.275412600
8	5.585014400	-1.943315500	1.947249300
3	-2.763279200	0.527781700	0.065164200
8	-3.225500500	2.163640300	1.199215900
8	-4.111086000	-0.728144300	0.964003800
8	-3.608559300	0.857377200	-1.718384700
16	-4.393094900	2.752224600	1.857640300
16	-5.534911000	-1.044109900	0.844857600
16	-4.762407600	1.614476500	-2.208798800
8	-5.585014400	1.943315500	1.947249300
8	-6.245434200	-0.474039000	-0.275412600
8	-5.367771600	2.556156300	-1.298158800

S2. Data used for lattice enthalpy estimations

The thermodynamics for the formation of $[\text{Li}_2(\text{SO}_2)_8][\text{B}_{12}\text{Cl}_{12}]$ in the solid state were investigated. Reaction enthalpies in the solid state were estimated by Born-Fajans-Haber cycles using the “volume-based” thermodynamics (VBT) approach to access lattice enthalpies (Table S1).¹ The total lattice potential energy, U_{pot} of a salt M_pX_q can be estimated from the formula unit volume, V_m , by:

$$U_{\text{pot}}(\text{M}_p\text{X}_q) = 2I (\alpha V_m^{-1/3} + \beta)$$

where V_m is the molecular volume (in nm^3), I is the lattice ionic strength, α and β are empirical constants. The lattice enthalpy ΔH_L was calculated by:

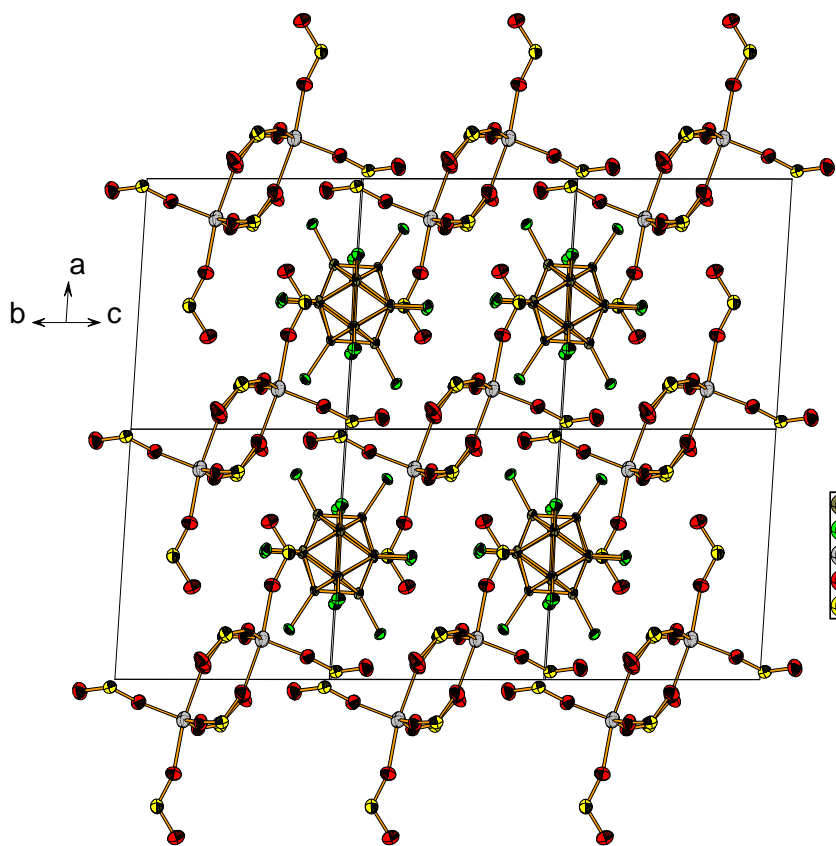
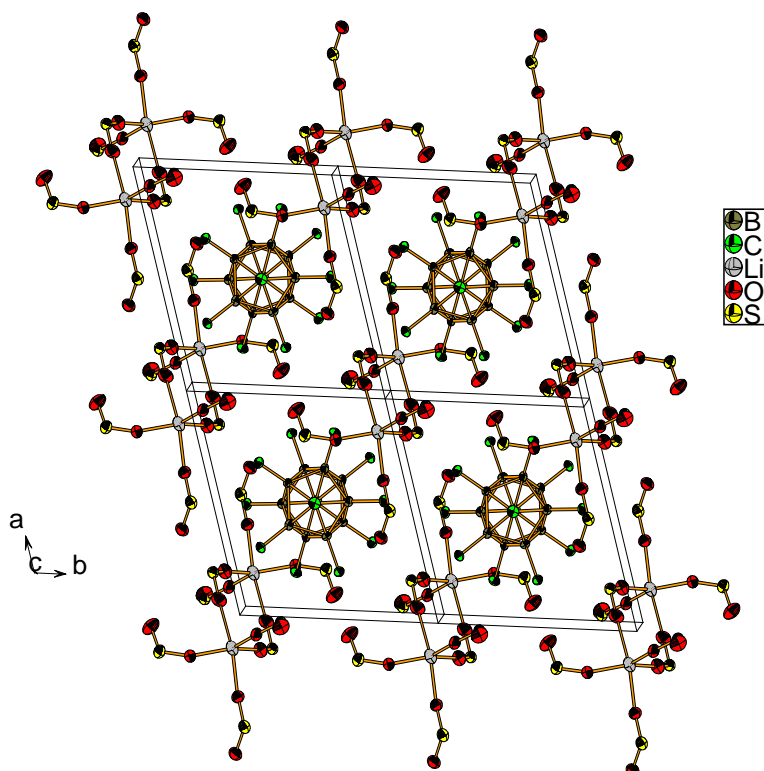
$$\Delta H_L = U_{\text{pot}}(\text{M}_p\text{X}_q) + [p(n_M/2-2) + q(n_X/2-2)] RT$$

where n_M and n_X are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for polyatomic nonlinear ions.

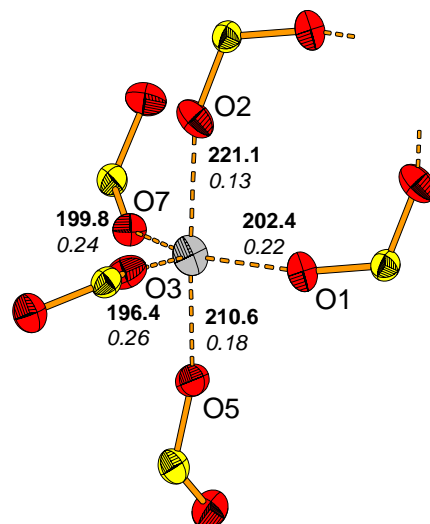
Table S1 Molecular volumes [nm^3] and lattice enthalpies [kJ/mol]

	V_m	H_L
$[\text{Li}_2(\text{SO}_2)_8][\text{B}_{12}\text{Cl}_{12}]$	0.9114	1482
$[\text{Li}(\text{SO}_2)_4]_2[\text{B}_{12}\text{Cl}_{12}]$	0.9114	851

S3. Solid state packing of $[\text{Li}_2(\text{SO}_2)_8][\text{B}_{12}\text{Cl}_{12}]$



S4. Coordination sphere around Li⁺ in [Li₂(SO₂)₈]²⁺



Section of the molecular structure of [Li₂(SO₂)₈]²⁺ showing the coordination environment around Li⁺ including bond distances [pm, **bold**] and valency units [v.u., *italics*]². Thermal ellipsoids are shown at the 50% probability level. Selected bond angles [°]: O2-Li1-O5 169.3(4), O1-Li1-O3 103.9(3), O3-Li1-O7 115.3(4), O7-Li1-O1 140.8(4), O1-Li1-O2 92.6(3), O1-Li1-O5 88.0(3), O3-Li1-O2 91.8(3), O3-Li1-O5 98.4(3), O7-Li1-O2 86.5(3), O7-Li1-O5 86.3(3). The apical Li-O distances are longer (av. 215.9 pm, 0.15 valency units (v.u.)²) than the equatorial Li-O distances (av. 199.5 pm, 0.24 v.u.). The sum of the bond valences around the lithium cation is 1.03 v.u. very close to the theoretical value of 1.

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1. a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore and L. Glasser, *Inorg. Chem.*, 1999, **38**, 3609, b) L. Glasser and H. D. B. Jenkins, *Chem. Soc. Rev.*, 2005, **34**, 866.
 2. The contacts (in valency units [v. u.]) have been defined as $s = \exp[(R_0 - R)/B]$, where R is the experimental distance, and R₀ and B are constants. (a) I. D. Brown, *The Chemical Bond in Inorganic Chemistry – The Bond Valence Model*, Oxford University Press, Oxford, 2002; (b) http://ccp14.sims.nrc.ca/ccp/web-mirrors/i_d_brown/bond_valence_param/.