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From icosahedron to a plane – flattening dodecaiodo-dodecaborate by successive stripping of iodine

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Abstract: It has been shown by electrospray ionisation-ion trap mass spectrometry that $B_{12}I_{12}^{2-}$ converts to an intact B_{12} cluster as a result of successive stripping of single iodine radicals or ions. Here we report the structure and stability of all intermediate $B_{12}I_n^-$ species ($n = 11$ to 1) determined by means of first-principles calculations. The initial predominant loss of an iodine radical occurs most probably via the triplet

state of $B_{12}I_{12}^{2-}$, and the reaction path for loss of an iodide ion from the singlet state crosses that from the triplet state. Experimentally, the boron clusters resulting from $B_{12}I_{12}^{2-}$ through loss of either iodide or iodine occur at the same excitation energy in the ion trap. We show that the icosahedral B_{12} unit commonly observed in dodecaborate compounds gets destabilized while losing iodine. The boron framework opens to non-

icosahedral structures with 5 to 6 iodines left. The temperature of the ions has a considerable influence on relative stability near the opening of the clusters. The most stable structures with 5 to 7 iodine atoms are neither planar nor icosahedral.

Keywords: Boranes, Computational chemistry, Density functional calculations, Mass spectrometry, Rearrangement

by aromaticity arguments, and has stressed the importance of non-icosahedral boron frameworks.^[6,7]

Thus, when an icosahedral dodecaborate with substituents at each B atom is stripped step-wise from its substituents, it must pass a degree of substitution where the icosahedral structure is energetically disfavored over open structures.

Recently, we could prepare B_{12} ions with any number of iodine substituents from 12 to 1, by fragmenting $B_{12}I_{12}^{2-}$ in an electrospray-ion trap mass spectrometer (ESI-MS).^[8] At the end of the fragmentation path, $B_{12}I_1^-$ loses a neutral B_{12} , leaving behind I^- (Figs. 1 and 2).^[8]

Introduction

Deltahedrons are the major structural motif of compounds with multiple B-B bonds. Icosahedra dominate molecular structures and modifications of the element.^[1] Interestingly, as predicted by simulations and then confirmed experimentally, the lowest-energy structure of a unit of 12 B atoms without further substituents is essentially planar (see Fig. 1).^[2-5] This has recently been rationalized

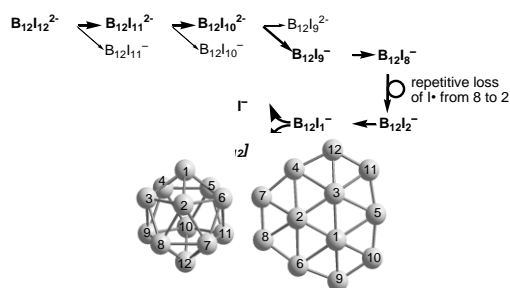


Figure 1. Top: Reactions of $B_{12}I_{12}^{2-}$ in ESI-tandem-MS. Major reaction pathways are shown in bold. For full details see ref. 8. Bottom: Icosahedral and planar structures, showing the B atom numbering used.

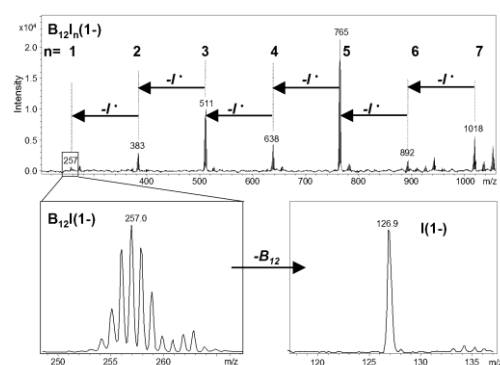


Figure 2. Partial mass spectrum of ions generated from $B_{12}I_{12}^{2-}$. Insets: Fragmentation of $B_{12}I_{11}^{-}$ and $B_{12}I_{10}^{-}$ under tandem-MS conditions. For full details, see ref. 8. For Br, Cl, F, or H as substituents, fragmentation occurs differently and leads to degradation of the B_{12} unit to smaller species.^[8,9] This difference could be associated with the lower electronegativity of iodine and the higher polarizability of the B-I bond, allowing electron donation from I into the boron clusters (SI Table S1), thus stabilizing the B_{12} structural motif. On B clusters, I acts as electron donor.^[10-11]

We therefore searched for the level of stripping at which the icosahedron is disfavored energetically over more open structures, a transition which requires major rearrangement of many atoms. We calculated all possible icosahedral and planar $B_{12}I_n$ structures (see Table 1) with $n = 11$ to 1 for icosahedra, and $n = 7$ to 1 for planes, minimized their energy, optimized their structure, and determined their relative stability for each given n .

Table 1. Number of possible isomers for icosahedral and planar structures

Number of substituents	icosahedral structures	planar structures	planar structures with enantiomers eliminated
11	1	4	3
10	3	22	14
9	5	76	43
8	12	165	90
7	14	312	142
6	24	312	166
5	14	264	142
4	12	165	90
3	5	76	43
2	3	22	14
1	1	4	3
0	1	1	1

Results and Discussion

In mass spectrometry of multiply charged negative anions (MCAs), decay can occur through three principle routes: loss of an electron, loss of an anion, and loss of a neutral unit.^[12] In the present study, we have not observed the loss of an electron in any of the fragmentations, but only loss of an anion or a radical/neutral or anionic atoms. This is in accordance with calculations showing that $B_{12}H_{12}^{2-}$ is the smallest electronically stable hydro-closododecaborate cluster.^[13] $B_6X_6^{2-}$ has been shown by calculations to be unstable to electron loss with $X = H$, but stable with $X = Cl$.^[14] Thus, the general pattern of fragmentation observed here for $B_{12}I_{12}^{2-}$, loss of neutral atoms and loss of ions, but not loss of electrons, agrees with previous calculations.

For $n = 12$ to 10, iodine can leave as radical or anion. At first glance, one would expect that the fragmentation pathway involving charge separation (i.e. loss of I^-) would be energetically favored, and indeed stability calculations support this estimation (the ionic pathway is favored over the radical by 149 kJ mol⁻¹, and still by 73 kJ mol⁻¹ when recombination of I^- to I_2 is considered). However, we found experimentally that both possible products, $B_{12}I_{11}^{2-}$ and $B_{12}I_{11}^-$, appear, but that the I^- fragmentation is preferred.^[5] For $n = 12$, we observed a 5:1 ratio in favor of the radical loss (Fig. 3), although energetically the loss of I^- is highly favored. $B_{12}I_{11}^{2-}$ and $B_{12}I_{11}^-$, started to appear at the same excitation energy applied in the ion trap and remained in a constant intensity ratio (Fig. 3). Thus, both products are probably generated simultaneously. Derivatives of the hydrogen-substituted cluster are fragmented in ESI-MS only to $B_{12}H_{11}^-$.^[5]

Comment [TD1]: Should the aromatic character of the B12 moiety be mentioned? - B.t.w. yes, I find this the right place for a short review.

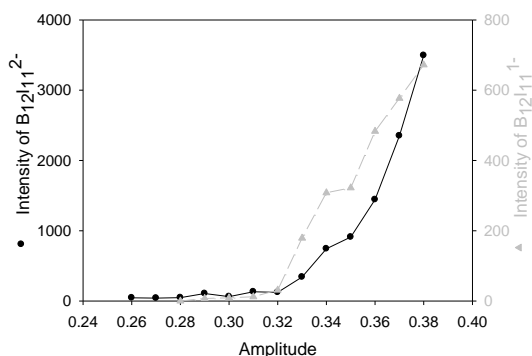


Figure 3. The yield of $B_{12}I_{11}^{2-}$ and of the sum of the products (including those from reaction with rest gases in the spectrometer) from $B_{12}I_{11}^{1-}$ are shown as a function of the amplitude with which the molecules were excited in the ion trap. $B_{12}I_{11}^{1-}$ reacts spontaneously with trace gases in the ion trap to adducts (for details see ref. 5); their individual intensities were added.

For $B_{12}I_n^{1-}$ ($n = 7$ to 2) there was no monotonic trend in the energy dependence for I loss (see Supporting Information). The data imply a comparatively low stability for $n=6$. This is in accordance with the mass spectrum shown in Fig. 2. There, maximal excitation of $B_{12}I_{12}^{2-}$ shows high intensities for $B_{12}I_5^{1-}$ and for $B_{12}I_7^{1-}$, but a low intensity for $B_{12}I_6^{1-}$. However, quantitative statements about the relative stabilities of the different ions cannot be drawn, as mass and degrees of freedom change during stripping of I.

The two product structures $B_{12}I_{11}^{2-}$ and $B_{12}I_{11}^{1-}$ do not differ much in their calculated geometries, except for the non-saturated boron which is pulled slightly deeper into the cluster (distance B1-B12 is 332 pm for the dianion and 317 pm for the monoanion, compared to 332 pm for $B_{12}I_{11}^{2-}$ and 342 pm for $B_{12}I_{12}^{2-}$). This corresponds to the experimental results of Peymann et al., who found the structure of $B_{12}Me_{12}^{2-}$ to differ less than 4 pm from that of its oxidation product $B_{12}Me_{12}^{1-}$.^[6]

A characteristic feature in the energetic treatment of MCAs is the presence of a “repulsive Coulomb barrier” (RCB), which arises “from the combination of the short range binding force with the purely repulsive long range Coulombic interaction”.^[12] RCBs can be considered for the detachment of electrons and anions; detachment of a radical does not lead to a potential minimum at large values of r , since the charge state of the MCA is not changed, and should thus be energetically unfavorable. RCBs can be identified with the transition states (TS) of fragmentation reactions of MCAs.

In order to understand both the simultaneous loss of I^- and of I^{\cdot} and the predominance of the radical loss, we estimated the position and energy of the respective TS by calculations with second order Møller-Plesset perturbation theory at Hartree-Fock optimized geometries.

The TS for the loss of I^- has a barrier of 384 kJ mol⁻¹ with a flat profile for B-I distances between 500 and 600 pm. The triplet state is less stable than the singlet state by 380 kJ mol⁻¹, but the shallow TS is reached by stretching the B-I bond only 40 pm from its equilibrium length (228 pm). Beyond the TS, the system dissociates into I^- and $B_{12}I_{11}^{2-}$. The two energy profiles must therefore intersect before the singlet state reaches the TS, and spin crossing will result

in the major product $B_{12}I_{11}^{2-}$. Spin crossings are forbidden by theory, but are common at elevated temperatures in the gas phase.^[15]

In order to estimate the position and energy of TS, we followed the loss of I^- and of I^{\cdot} in calculations with second order Møller-Plesset perturbation theory at Hartree-Fock optimized geometries.

We have modelled the fragmentation to the minor, singlet state products, I^- and $B_{12}I_{11}^{1-}$, starting from the singlet electronic state of the parent $B_{12}I_{12}^{2-}$ cluster. In this case we calculated a very late transition state, with a B-I bond stretched up to 540-600 pm, and a high energy barrier of 384 kJ mol⁻¹. On the other hand, the fragmentation to the major products, I^{\cdot} and $B_{12}I_{11}^{2-}$, was modelled via the triplet state of $B_{12}I_{12}^{2-}$ and the calculations reveal that a shallow transition state is reached very fast, at B-I distance only 40 pm longer than the equilibrium bond length (228 pm), beyond which the cluster readily dissociates to two doublet state species. The two energy profiles must therefore intersect before the singlet state reaches the TS, and spin crossing will result in the major product $B_{12}I_{11}^{2-}$. Spin crossings are forbidden by theory, but are common at elevated temperatures in the gas phase.^[15] A more detailed exploration of the mechanism of all possible reactions concerning the fragmentation of $B_{12}I_{12}^{2-}$ requires more elaborate and expensive calculations and is beyond the scope of the current study.

The long B-I distance required for overcoming the activation barrier when iodine leaves as anion can be partly explained by the peculiar charge distribution within the iodinated *closo*-dodecaborates as calculated by Natural Population Analysis (NPA). According to this analysis, the B_{12} icosahedron itself carries the most of the negative charge, whereas the I substituents are slightly positive or only slightly negative, depending on the computational software used (see Tables S1 and S1a for a detailed comparison). When the B-I bond is broken heterolytically to form $B_{12}I_{11}^{1-}$, the I atoms on the cluster lose electron density. This might be the reason that the leaving I^- is attached to the parent cluster, counteracting any electrostatic repulsion between the two anions.

The derivatives of $B_{12}I_{10}$ and $B_{12}I_9$ with charges of 2- (obtained after loss of I^{\cdot}) are more stable than the corresponding ions of charge 1- by 123.2 kJ mol⁻¹ and 12.8 kJ mol⁻¹, respectively. Independent of the charge, the most stable derivatives with 10 I atoms have lost the I atoms on B-1 and B-2, and in addition on B-12 for $B_{12}I_9$.

In ESI-MS, $B_{12}I_7^{1-}$ shows exclusively the successive loss of I^{\cdot} , while for more than 7 I atoms, reactions with rest gases in the spectrometer are observed,^[8] possibly indicating rearrangement of $B_{12}I_7^{1-}$ to a non-icosahedral structure. As also our initial calculations indicated that the transition from icosahedral to open geometry should occur for $B_{12}I_n^{1-}$ with n between 5 and 7, we calculated the geometries and energies of all possible icosahedral isomers with 0 to 12 I atoms, and of all planar structures with 7, 6 and 5 I atoms (142, 166, and 142 isomers, respectively, not considering enantiomers) (see Table 1).

The internal energies of individual ions in an ensemble of ions generated in ESI-MS can reach values of 100-200 kJ mol⁻¹, corresponding to thermal energies of some 1000 K.^[16] We therefore calculated the Gibbs free energies, ΔG , for $B_{12}I_n^{1-}$ with $n = 0-7$ for 0 K, 1200 K, and 5000 K, using the ideal-gas approximation for the isomers representing the minimum of the potential energy at 0 K.

Comment [VN3]: I still feel a bit uncomfortable with this explanation. I took it from the text above, but I don't really get it. But if you are sure that it's correct, just keep it.

Comment [TD2]: I think it is important to introduce the RCB concept here, as it belongs to the „special considerations“ concerning multiply charged ions which the referee points to. – I changed the first sentence of the following paragraph somewhat to get a better connection to the present one.

The computed free energy differences, $\Delta G = G_{\text{icosahedron}} - G_{\text{open}} = \Delta U + RT - T\Delta S$, are shown in Fig. 4.

For the B₁₂ clusters with 6 and 7 I substituents, the temperature dependence of ΔG is important. At 0 K, a B₁₂ icosahedron with 6 or 7 I substituents is favored by 20 or 50 kJ mol⁻¹, respectively (Fig. 4). Increase in temperature was found to destabilize the icosahedral configuration for these species with respect to the more open ones, as the vibrational contributions to U are larger for icosahedra than for open structures, and S is smaller, increasing the internal energy of the icosahedral isomers. At the highest temperature studied (5000 K, which might be considered unrealistically high), the thermal contributions to G dominate over the potential energy, rendering the open derivatives more favorable, by 45 and 84 kJ mol⁻¹, resp., than their icosahedral counterparts (Fig. 4). For a realistic temperature of 1200 K, the more open structure is favored by 4 kJ mol⁻¹ for n=6, the icosahedral structure is favored by 13 kJ mol⁻¹ for n=7.

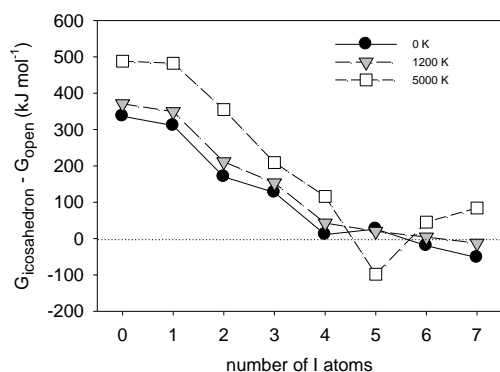


Figure 4. Free energy difference between the lowest-energy icosahedral and open isomers of B₁₂I_n⁻ with n = 0-7, for T = 0, 1200 and 5000 K. Lines are guide-to-the-eye. For points below the dotted line, the icosahedral structure is more stable than open structures.

For n = 0 to 4, open structures are more stable than icosahedral structures at all temperatures investigated, the icosahedron being disfavored due to higher internal energy and lower entropy. The lowest-energy B₁₂I_n⁻ isomers with n = 1-5 are planar, with I attached to peripheral B atoms only (Fig. 5).

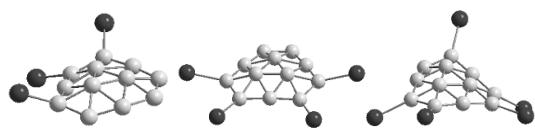


Figure 5. Structures of the most stable B₁₂I_n⁻ with n = 3 to 5.

For B₁₂I₅⁻, the internal energy is lower, but the entropy is higher for the plane compared to the icosahedron. With increasing temperature, ΔG of the icosahedron becomes more negative (+26, +20 and -98 kJ mol⁻¹ at T = 0, 1200 and 5000 K, resp.), stabilizing the icosahedral configuration at the highest temperature. The calculated IR spectrum of the quasi-planar B₁₂I₅⁻ contains two vibrational modes with very low frequencies (≤ 15 cm⁻¹) and zero intensity (at 0 K), corresponding to out-of-plane bending of 4 of the

5 I atoms and their B atoms. At elevated temperatures these vibrations are more pronounced, destabilizing the planar B₁₂I₅⁻.

The B₁₂I₅⁻ isomer with second-lowest energy is less stable by only 4 kJ mol⁻¹ and is no longer planar (see Movie S3 in Supporting information). In geometry optimizations of planar B₁₂I₆⁻ and B₁₂I₇⁻, planarity is lost. The most stable B₁₂I₆⁻ derived from a plane is a partly open icosahedron (Fig. 6), and the most stable open B₁₂I₇⁻ species also has icosahedral features (Fig. 6). Isomers intermediate in structure between icosahedron and plane are energetically accessible already for n = 6 at 1200 K, and at 5000 K for n = 7.

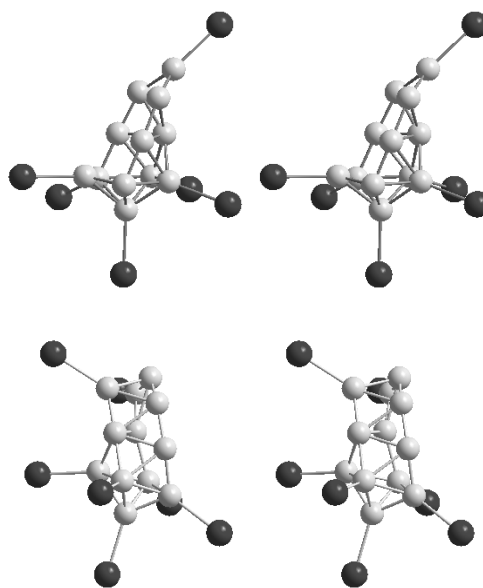


Figure 6. Stereo pictures of the most stable B₁₂I₆⁻ derived from a planar structure (top) and the most stable B₁₂I₇⁻ at 5000 K (bottom).

For B₁₂I_n⁻ with n = 5 and 6, we found structurally very different isomers with very similar energies. As flat B clusters carry a large degree of fluxionality,^[6,7] a mixture of structures can be expected in the experiment. In our search, we allowed only icosahedral or quasi-planar starting structures.

Conclusion

The two configurations discussed in the literature for a dodecaboron unit, icosahedron and plane, have previously been considered only as isolated, and structurally orthogonal entities. We have shown here, for the first time, that the icosahedral structure of a partly substituted dodecaborate is no longer stable when five or less substituents are present on the cluster. For six and seven substituents, temperature determines the relative stability, and energetically accessible isomers being neither icosahedral nor planar were found.

If iodine was always lost to form the thermodynamically most stable structures, rearrangements would have to occur when the

sixth I atom is lost. These could be diamond-square-diamond rearrangements,^[15] or 1,2-suprafacial migration of I. We have shown that kinetic factors must be taken into account when predicting the possible path of the stripping. Structures intermediate between icosahedra and planes might be possible, and as B clusters are known to be fluctuating,^[6,7] it appears impossible to establish an unambiguous reaction route. The flexible nature of some clusters is evident from the movies in the Supporting information showing the course of minimization of planar structures and molecular dynamics of the lowest-energy $B_{12}I_6^-$.

The $B_{12}I_n$ ($n < 12$) species discussed here are only accessible by gas-phase reactions. Our attempts to identify such species in a mixture obtained from $Cs_2B_{12}I_{12}$ by controlled thermal decomposition to 30% weight loss (which finally leads to amorphous material^[18]) failed.

This is, however, different for reactions in the gas phase where iodine can leave as a radical and the species are more isolated. It would be challenging to record photoelectron or IR spectra of some of the clusters which we have identified in mass spectrometry, in the manner described previously for bare boron clusters,^[5] complementing the computational results presented here.

Experimental Section

ESI-MS measurements were performed on a Bruker Esquire-LC ion trap mass spectrometer (Bruker Daltonik, Bremen, Germany). The $B_{12}I_{12}^{2-}$ salt (counter ion sodium or tetraalkylammonium) was dissolved in acetonitrile (LCMS grade; VWR, Darmstadt, Germany) at concentrations of approximately 10^{-5} – 10^{-6} mol L⁻¹ and injected into the mass spectrometer via a syringe pump at a flow rate of 3 μ L min⁻¹. Spectra were recorded in the negative ion mode for three to five minutes and averaged. Collision-induced dissociation (CID) in the nozzle-skimmer region (skimmer-CID, sCID) as well as tandem-MS were used to induce reactions of the sample ions in the mass spectrometer. For detailed instrument parameters see ref. 5. In tandem-MS experiments, ions with a defined m/z-value were isolated and specifically activated by collisions with the background gas (mainly He, and some N₂ and H₂O) in the ion trap. The collision was induced by applying an adjustable ac voltage to the ion trap end caps. Stepwise increase of the ac amplitude and observation of the relative product ion intensities allowed to compare the relative activation energies for different fragmentation pathways.

With the exception of the cluster-only total charge calculations, DFT calculations were performed by means of ADF 2010,^[19] using all-electron basis sets of TZP quality and accounting for scalar relativistic corrections (ZORA formalism). Full geometry optimizations were carried out employing the BP86 functional (BP/ZORA/TZP), followed by single point calculations at the B3LYP level (B3LYP/ZORA/TZP).

The cluster-only total charge (CTC) was obtained by summing all calculated individual cluster atoms Natural Population Analysis (NPA) charges, which were computed at the B3LYP/6-311+G(2d,p) level for all atoms except for iodine, which was calculated using B3LYP/6-311+G(d) basis set.

All isomers were confirmed as local minima using the harmonic approximation, and the resulting frequencies were employed to compute the relative free energies, ΔG . The latter were calculated within the ideal-gas approximation by using the relation $\Delta G(T) = \Delta U(T) + RT - T\Delta S(T)$, where R is the universal gas constant, T is the temperature, S is the entropy and U is the internal energy including the potential energy, the zero-point energy correction and the thermal contributions. To study the process of elimination of the first iodine from $B_{12}I_{12}^{2-}$, we performed MP2 single point calculations on Hartree-Fock optimized geometries, employing 6-311+G(d) and 6-311G* basis sets for boron and iodine, respectively. The reaction pathways were estimated by restricted geometry optimizations (at the Hartree-Fock level), keeping one B-I distance frozen. These calculations were carried out by means of Gaussian 03.^[20]

Born-Oppenheimer Molecular Dynamics (BO-MD) simulations were performed at the PBE/DZVP-GGA level, employing deMon2k,^[21] starting from the minimum geometry, with random velocities assigned to the atoms. NVT calculations at $T = 300$ and 600 K (Nosé-Hoover chain thermostat) were carried out for 10 ps.

Acknowledgements

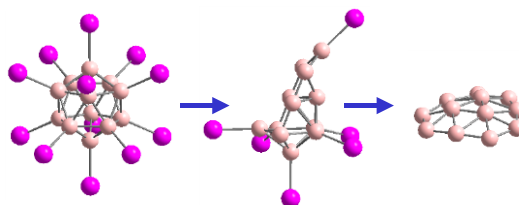
This work was supported by Spanish Ministerio de Ciencia e Innovación (CTQ2010-16237), CSIC (I3P grant to P.F.), the Generalitat de Catalunya 2009/SGR/00279 and the Center for Functional Nanomaterials (NanoFun) of Jacobs University Bremen. Access to the High Performance Computing Centre of CSIC and Centre de Supercomputació de Catalunya (CESCA) is gratefully acknowledged.

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Flattened icosahedra

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Gabel**..... Page – Page

**From icosahedron to a plane –
flattening dodecaiodo-
dodecaborate by successive
stripping of iodine**



When icosahedral $B_{12}I_{12}^{2-}$ is fragmented in mass spectrometry and its iodine atoms are stripped off one by one, it will eventually form a planar B_{12} unit. This transition occurs when 7 to 5 iodine atoms remain.