UNIVERSITAT DE BARCELONA
Química Inorgànica

Notícies Inorgàniques

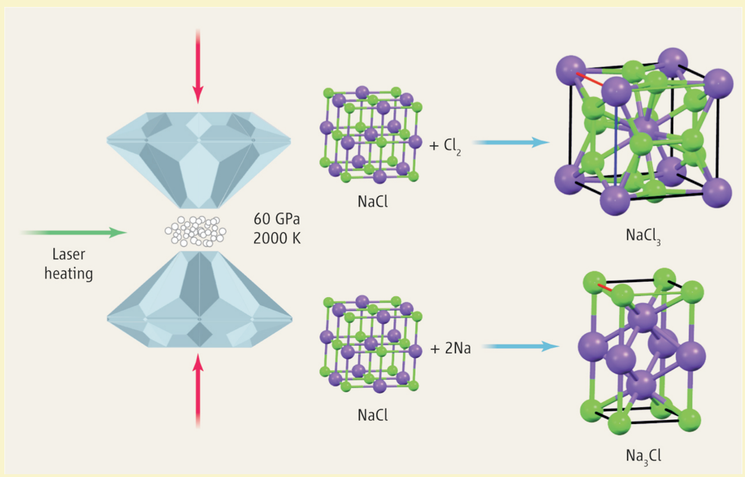
Any 13, Núm. 66, Febrer de 2014

http://www.ub.edu/inorgani/dqi.htm

Editors: Gabriel Aullón, Ramón Bosque i Joaquim Sales. Correspondència: noticies@qi.ub.edu

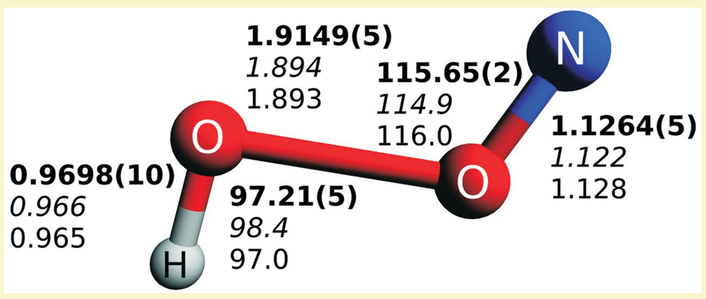
La sal prodigiosa

The conventional wisdom about sodium chloride assumes that it has a one-to-one ratio of sodium and chlorine. But at high pressures, that conventional wisdom breaks down. A new study (A. R. Oganov et al., *Science,* **2013**, *342*, 1502. DOI: 10.1126/science.1244989) reports that at high pressure sodium and chlorine can combine with different stoichiometries. The researchers used a quantum mechanical algorithm to predict structures of various combinations of sodium and chlorine at pressures ranging from 20 to 200 gigapascals: Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$, and $NaCl_7$. Appropriate conditions can exist within Earth, but such compounds are more likely found elsewhere in the universe. To test the predictions, the researchers synthesized Na_3Cl and two forms of $NaCl_3$ by placing NaCl in a diamond-anvil cell with excess sodium or chlorine at high pressure. With the exception of one form of $NaCl_3$, which is a semiconductor, all the compounds are metals. The semiconducting form of $NaCl_3$ contains linear trichloride units. The crystal structure of $NaCl_7$ is similar to that of metallic $NaCl_3$, except that chlorine and sodium are in central positions, respectively. The structure of Na_3Cl consists of sodium layers that alternate with insulating NaCl layers and temperature.



L'oxigen s'allarga

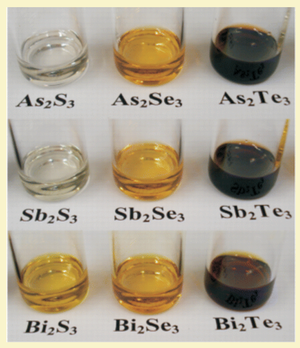
A team(M. C. McCarthy et al., *Science*, **2013**, *342*, 1354. DOI: 10.1126/science.1244180) has isolated a previously undetected molecule and found that it has the longest oxygen-oxygen bond yet discovered. Researchers have long known that nitrous acid (HONO) plays an important role in atmospheric chemistry. But most people dismissed the existence of the compound's isomer, nitrosyl O-hydroxide (HOON), predicting that it wouldn't be stable. Still, earlier this year a computational study suggested HOON's plausibility at low temperatures. The group generated trans-HOON by combining nitric oxide, water vapor, and neon; applying an electrical discharge to the mix; and then cooling the resulting products with a method called supersonic expansion. The researchers detected the never-before-seen HOON with microwave spectroscopy and determined its O–O bond length to be 1.9 Å, 32% longer than a standard O–O single bond, such as the one in hydrogen peroxide (HOOH).



HOON has an O–O bond that's 32% longer than the one in hydrogen peroxide and 58% longer than the double bond in molecular oxygen

Semiconductors en solució

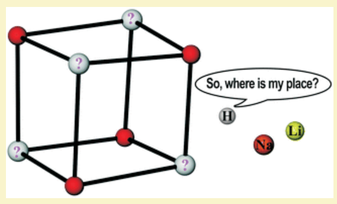
Semiconductors, thanks to their controllable and highly customizable electronic properties, function as control centers in most of today's high-tech devices. Typically, these devices are manufactured via expensive and energy-consuming vacuum deposition methods. Solution-phase processing—simply and inexpensively spraying a thin film of semiconductors, for instance, instead of using a complex vacuum-based process to deposit them—would be a major improvement. But nearly all solvents are ineffective at dissolving semiconductors. Now it has benn reported (R.L. Brutchey et al., *J. Am. Chem. Soc*. **2013**, *135*, 15722. DOI: 10.1021/ja4084336). that a largely unexplored, "relatively nonhazardous" two-component solvent readily dissolves a family of semiconductors. Specifically, the team finds that at room temperature and under ambient pressure, a mixture of 1,2-ethylenediamine and 1,2-ethanedithiol can rapidly dissolve bulk samples of metal chalcogenides, binary semiconductors. They found that the mixed solvent could be used to make highly concentrated (21–32% by weight) solutions of several metal chalcogenides, including As_2S_3, As_2Se_3, As_2Te_3, Sb_2S_3, Sb_2Se_3, and Sb_2Te_3. In an initial test of the solvent's usefulness for processing semiconductors, the team prepared thin films by spin coating the liquids on a support material and rapidly heating to evaporate the solvent.

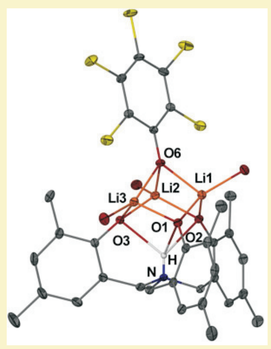


A thiol and amine mixture at room temperature dissolves at least nine semiconductors, a finding that could lower processing costs for thin-film applications.

És l'hidrogen un alcalí?

For the first time, scientists have shown that hydrogen can stand in for alkali metals in typical alkali metal structures. Hydrogen, having just one s electron, is chemically analogous to group 1 alkali metal. However, the two exhibit pronounced structural differences under ambient conditions. This is clearly shown by hydrogen being a gas and the group 1 elements being reactive solid metals at room temperature and pressure. While some similarities have been demonstrated, in particular with lithium, the smallest and lightest group 1 metal with the most covalent character, comparable participation of hydrogen in the solid state has remained unverified. Now, (M. Davidson et al., Chem. Commun., **2013**, *49*, 11809. DOI: 101.1039/c3cc47393g) have devised an organometallic synthetic strategy to make pseudocubane motifs of ammonium tris(phenol) ligands and lithium or sodium atoms, where one of the metals has been replaced by a hydrogen atom. The hydrogen forms the rarely reported trifurcated 4-centre hydrogen bond. Such an arrangement is not uncommon for the larger alkali This work confirms hydrogen's position at the top of group 1 and seems likely to stimulate further debate and discussion.





Hydrogen can stand in for alkali metals in typical alkali metal structures

Breus

• Fa cent anys que Frederick Soddy (1877-1956), guardonat amb el Premi Nobel de Química l'any 1908, va proposar el concepte d'isòtop, per expressar que els elements podien tenir més d'un pes atòmic. Ho féu en una carta a l'editor de **Nature**, publicada el 4 de Desembre de 1913. (*Chem. Emg. News*, **2013**, *91* (48), 30)

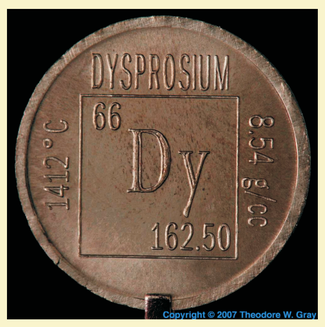
•En commemoració del centenari de la concessió el 1914 del Premi Nobel de Física a Max von Laue, en descobrir que els cristalls difractaven els raigs X, el passat 20 de gener es va inaugurar a París, el «International Year of Crystallography (IYCr2014)» (www.iycr2014.org).

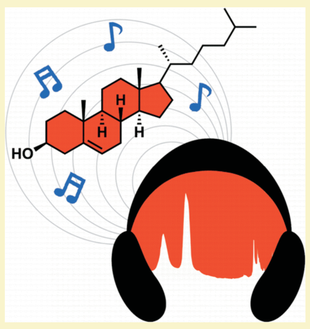
•La «Food and Drug Administration» (FDA) dels EUA, ha acordat prohibir els greixos parcialment saturats, anomenats greixos trans, que són molt presents en els menjars preparats. (*Chem. Eng. News.*, **2013**, *91 (46)*, 8.

Avui recomanem

El programari MOLinsigh, de la Universitat Nova de Lisboa, que converteix els espectres IR al format MIDI, de manera que poden escoltar-se. La intensitat del pic, a l'eix y, es representa pel to, i una nota alta indica un senyal més intens. La freqüència, a l'eix x, representa el temps. De manera que pot assignar-se un determinat so a un grup funcional. Vegeu *J. Chem. Ed.*, **2013**, *90*, 1028.

L'element





L'element número 66, **disprosi**, fou descobert pel químic francès Paul Emile Lecoq de Boisbaudran l'any 1886 com a una impuresa de l'òxid d'erbi; el nom prové del terme grec "δψσπροσιτοσ" (*dysprositos*) que vol dir "difícil d'obtenir". Com la resta de lantànids es troba en els minerals monazita i bastnäsita en quantitats petites però suficients per poder-lo extreure. No fou aïllat fins els anys 50, quan es popularitzaren les tècniques de separació per intercanvi iònic. La producció mundial és de l'ordre de 100 Tm anuals .

L'element té aspecte metàl·lic que recorda la plata, és relativament estable a l'aire a temperatura ambient i és prou tou per poder-se tallar amb un ganivet.

El disprosi natural té set isòtops estables – sent el més abundant el ^{162}Dy amb un 26.5% –, només el ^{156}Dy es desintegra amb emissió de partícules α, però té una vida mitjana de 10^{18} anys.

Les principals aplicacions és com a component d'aliatges que són bons imants permanents i en la indústria nuclear com a composites que absorbeixen neutrons, i també en dosímetres per mesurar la quantitat de radioactivitat. El DyI_3 s'empra en la fabricació de làmpades de descàrrega, l'halur es dissocia al centre calent de la bombeta i el disprosi format absorbeix energia que emet en forma de llum visible.