# Kurze Mitteilungen

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## The Centenary of the Discovery of Ytterbium by *Marignac* in Geneva 1878*

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*Abstract*

The historical context of the discovery of ytterbium, and a few specific features of subsequent studies of this element, are shortly discussed.

The two or three elements discovered in Switzerland are all lanthanides and have all been found at the University of Geneva. The somewhat debatable among the three cases is *holmium* for which evidence from narrow absorption bands were presented by Soret 1878, but the general consensus is that this element was established by Cleve in Uppsala in 1879, at the same time as thulium. It is not open to doubt that Marignac discovered *gadolinium* in 1880 [1, 2] and *ytterbium* in 1878 [3, 4] though it must be added that the first sesquioxide samples prepared contained minor admixtures of adjacent elements. Whereas thulium since 1887 was suspected for consisting of two or three elements, but the patient and careful fractional crystallization of $[Tm(OH_2)_9](BrO_3)_3$ by *James* [5] finally disproved this hypothesis, the situation was the opposite with ytterbium, containing small amounts of the subsequent element. We do not here describe the extended polemic of priority (stretching between 1907 and 1910) between Carl Auer von Welsbach calling the two elements aldebaranium and cassiopeium, and Georges Urbain calling them neo-ytterbium and lutetium. Since 1945, the latter name has prevailed, together with ytterbium originally proposed by Marignac for the major constituent.

*Jean-Charles Galissard de Marignac* was born in Geneva 24. April 1817, went to Paris and became student, first at Ecole Polytechnique 1835, and then at Ecole des Mines. He returned to Geneva in 1841, where he was appointed "professeur de chimie minérale et de minéralogie à l'Académie de Genève", a post he retained to 1878. Though he sometimes travelled in Europe (thus, he spent some time with *Liebig* in Giessen) he stayed in Geneva, when he retired, and died there the 16. April 1894.

Marignac was a remarkable pioneer in the understanding of inorganic chemistry during a large part of last Century. He is probably best known for exceedingly accurate determinations of equivalent weights by gravimetric methods. When Avogadro's hypothesis became generally accepted (after the Congress in Karlsruhe 1860) the corollary of reliable atomic weights formed the basis for the Periodic Table in 1869. Like *Mendelejev* was fully convinced that a more fundamental parameter (such as $Z$) subsists behind the Periodic classification, Marignac was attracted by *Prout*'s idea of integers multiplied by the atomic weight of hydrogen, but had regretfully to admit that the facts only had a most unexpected statistical bias in this direction, though he suggested the conceivable existence of isotope mixtures. Among the research related to Avogadro's hypothesis may be mentioned his demonstration of ozone being a triatomic molecule. This work, as well as studies of hydrates of sulphuric acid, have had long-lasting effects on chemistry in Geneva. Marignac also established interesting cases of isomorphic salts, not only of $SiF_6^{-2}$, $TiF_6^{-2}$, $ZrF_6^{-2}$ and $SnF_6^{-2}$ but also of $NbOF_5^{-2}$ (and is a precursor to *Alfred Werner*

at this point) and prepared dodekatungstosilicic acid, hydrated $H_4SiW_{12}O_{40}$, in 1862.

Marignac started work on rare earths in 1840, and continued intermittently along this line the rest of his life. The general opinions about rare earths reached a certain plateau in 1843, when *Mosander* recognized yttrium, lanthanum, cerium, didymium (shown in 1885 by *Auer von Welsbach* to be a mixture of Pr and Nd), terbium (highly impure) and erbium. It is not generally recognized that Gladstone [6] three years before the paper on spectral analysis by *Bunsen* and *Kirchhoff* noted the narrow absorption bands (similar to *Fraunhofer* lines) of didymium salts in crystals, glasses and in solution, and as recently reviewed [7] also the candoluminescence of incandescent oxides (heated in flames) early attracted attention. Some of the trivalent lanthanides produce narrow emission bands corresponding to characteristic colours (Ho mauve, Er emerald-green and Tm deep purple) which cannot be obtained from the standard temperature—dependent emission spectrum of opaque ("black-body") objects. Whereas *Soret*, and later *Joye*, exploited spectroscopic observations in Geneva, Marignac used more conventional chemical techniques for the separation of Yb, and in particular the fractional pyrolysis of molten nitrates, where the tendency toward formation of insoluble basic salts increases in direction from the colourless yttrium toward the pink erbium salts, followed by the colourless ytterbium, corresponding to decreasing ionic radii, and increasing *Brønsted* acidity of the aqua ions.

At the time of Marignac, ytterbium(III) salts were considered colourless in the strong sense that no absorption bands were observed. Much later, the band in the near infra-red at 970 nm ($10300$ cm$^{-1}$) was identified with the transition from the groundstate $^2F_{7/2}$ of the configuration $4f^{13}$ (lacking only one of the fourteen possible 4f electrons) to the only other level $^2F_{5/2}$. Since the transition energy consists almost exclusively of spin-orbit coupling, this observation was used by *Gobrecht* [8] to interpolate the variation in the trivalent lanthanides, allowing the *J*-levels of the lowest multiplet to be identified, though the conspicuous variation [9] with oxidation state in isoelectronic bivalent species shows that the *Sommerfeld* formula with a definite screening constant is not a perfect approximation. On the other hand, atomic spectra of Yb and Yb$^+$ obtained in arcs and sparks were used early to detect the element, and to detect admixtures of the adjacent elements Tm and Lu. In this connection, it is interesting to note the weak variation of the spin-orbit separation $10214$ cm$^{-1}$ in Yb$^{+3}$ [10] relative to $10149$ cm$^{-1}$ in the excited configuration $4f^{13}6s^2$ of Yb$^+$ (with the levels $21419$ and $31568$ cm$^{-1}$ above the groundstate belonging to $4f^{14}6s$) to be compared with values situated between $10100$ and $10200$ cm$^{-1}$ in Yb(III) compounds when corrected for weak "ligand field" effects. The variation is even smaller between $8771.25$ cm$^{-1}$ in the

lowest configuration $4f^{13}6s^2$ in the gaseous thulium atom and $8774.02$ cm$^{-1}$ in $4f^{13}$ in Tm$^{+2}$. The excited state of Yb(III) in vitreous and crystalline solids has great importance for energy transfer (with possible application to lasers) and infra-red to visible up-conversion [11]. One of the more unexpected features of absorption spectra of undiluted ytterbium(III) compounds are very weak bands in the green around $21000$ cm$^{-1}$ of $Yb_2O_3$ and YbOF [12] corresponding to the simultaneous excitation of two adjacent Yb(III), in analogy to the simultaneous quartet-doublet excitations of two Cr(III) producing narrow absorption bands of the ruby in the near ultra-violet.

Not only the atomic spectra show that ytterbium is a *spectroscopic alkaline earth* [13] but also the excited states of diatomic molecules such as YbH and YbCl. Nevertheless, solid $YbCl_2$ was first prepared [14] in 1929 and shown to be diamagnetic, indicating the closed-shell $4f^{14}$. About the same time, Yntema exploited the low solubility of $YbSO_4$ formed by electrolysis for separation from neighbour elements. Whereas metallic ytterbium also is diamagnetic and is barium-like in other aspects, such as the larger molar volume than lanthanum-like metals, *Klemm* demonstrated later that many ytterbium alloys contain paramagnetic $4f^{13}$ Yb(III). The *photo-electron spectrum* of metallic Yb also shows two 4f signals at 6.0 eV lower ionization energy than metallic Lu [15] whereas the multiple signals due to $4f^{13} \rightarrow 4f^{12}$ ionization of non-conducting Yb(III) solids systematically start 1 to 1.5 eV below the two signals in analogous Lu(III) compounds. These observations can be incorporated into considerations about *Kossel* isoelectronic series [16, 17], but it is perhaps more interesting to the chemist that the *Mulliken* electronegativity (defined as the average value of the ionization energy and the electron affinity of the partly filled shell) is almost the same, $(14 + 6)/2$ for Yb(III) and $(12 + 10)$ eV/2 for Cu(II) in spite of the obvious fact that the chemistry of copper(II) corresponds to much more covalent behaviour, also when compared with Ni(II) and Zn(II) [18], whereas the chemical properties of Yb(III) interpolate smoothly between Tm(III) and Lu(III). The "isolation" of a partly filled shell seems to be a function of the ratio between the ionic radius and the average radius of the partly filled shell, and seen from this point of view, Yb(III) may represent the most extreme case known, until 5 g group compounds are prepared. It is a major dilemma for "ligand field" arguments [18, 19] that the lowest ionization energy of the 4f shell is *higher* than of the loosest bound ligand orbitals (consisting for instance, of oxygen or fluorine 2p) and the two elements discovered by Marignac, Gd(III) and Yb(III), have been particularly significant in this sense. A spectroscopic difference between Yb(III) and most other trivalent lanthanides is the *electron transfer bands* [20–22] at slightly higher wave-numbers than in europium(III) complexes of the same set of ligands, cul-

minating in purple $YbI_6^{-3}$ [23] and green $Yb(C_5H_5)_3$ [24]. The corresponding Er(III) iodide and cyclopenta-dienide complexes are pink, due to the much weaker transitions to excited $J$-levels of $4f^{11}$. The crystal structures with highly varying coordination number $N$ from 3 to 16 were recently reviewed by *Flahaut* [25] and by *Sinha* [26].

It is difficult today to imagine exactly how chemistry appeared to somebody born 160 years ago. Marignac was a seriously and obstinately working chemist, hoping for understanding by induction, but without false illusions about a deductive theory. Whether it was by preference or by necessity, he never had any direct collaborators, and he worked in a modestly equipped and rather dim laboratory in the "Bastions". He retired before the magnificient building in Boulevard des Philosophes was inaugurated, and according to *Mary Elvira Weeks* [27], he suffered from a bad heart condition the last ten years, and had to stop active work shortly after the discovery of gadolinium. Marignac is an attractive personality from before the time when being numerous became an axiomatic virtue, and his example also serves to warn us against sacrificing quality to quantity.

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