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History of Chemistry

Studies on Gadolinium in Geneva since its Discovery by *Marignac* in 1880*

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Abstract

Hundred years ago, *Marignac* characterized the new element gadolinium in its oxide. Many chemists and physicists at the University of Geneva have worked on the optical and magnetic properties of metallic gadolinium, its alloys, compounds and diluted Gd(III) substituted on various sites in crystals and glasses. Their results of investigating absorption, luminescence and photo-electron spectra, as well as paramagnetic resonance, are put in a context of contemporary studies elsewhere, and the theoretical interpretation and its implications are shortly discussed.

Two years ago, the discovery of ytterbium by *Marignac* in 1878 was commemorated in this journal [1]. The following year, the centenary of Ecole de Chimie and its building (used for 92 years) in Boulevard des Philosophes was celebrated [2] and in a paper on the early history of chemistry in Geneva, a photo of Marignac was included [3]. Though Marignac retired (for health reasons) 1878 from the post as professor at the Academy (since 1876 University) of Geneva, he had occupied since 1841, he discovered in 1880 his second rare earth [4] by careful recrystallization of the potassium double sulphates $K_3Ln(SO_4)_3$. This technique is tedious because the salt at each fractionation has to be decomposed by KOH to $Ln(OH)_3$ to be filtered off. The determination of atomic weights, in which Marignac was one of the two or three greatest experts [2,5,6] was perturbed by the presence of variable amounts of yttrium (89) in this region of the fractionation according to ionic radii, whereas it had been very useful in characterizing ytterbium (172) and erbium (168). It may be noted that Marignac [6] gives the weight of the oxide containing 16 g oxygen, e.g. 128 corresponds to the atomic weight 168. The least soluble double sulphates contain a mixture of neodymium and the adjacent elements (such as samarium discovered by *Lecoq de Boisbaudran* 1879) but an intermediate fraction (solubility between 5 and 10 g/l saturated K_2SO_4) had a well-defined atomic weight 157.2 (present value for gadolinium 157.25) and formed a colourless oxide. The subsequent, more soluble sulphate fractions contain mixtures of yttrium, dysprosium and terbium.

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Marignac did not want [4] to suggest a definite name for his new element, but called it provisionally $Y\alpha$, the first member of the closely similar yttrium group. In 1886, Lecoq de Boisbaudran (who also isolated gallium in 1875) took up the study of the rare earths chemically related to yttria, and confirmed Marignac's findings, and suggested the name *gadolinium* (which was accepted [5] by Marignac). Before 1944, it was not the custom to name elements after famous scientists (such as the synthetic transamericium elements with $Z = 96$ and 99 to 105) and the name really went into chemistry via the mineral gadolinite ($Ln_2Be_2FeSi_2O_{10}$) containing both beryllate and silicate anions, which got its name after the Finnish chemist *Johan Gadolin* who in 1794 extracted from it an oxide mixture ("rare earth") having Y_2O_3 as the major constituent (these studies were continued [7] mainly by *Berzelius* and *Mosander*). By the same token, samarium derives its name from the mineral samarskite (discovered by a Russian colonel) and used by Marignac [4,6].

Though gadolinium salts do not show any absorption bands in the visible (in contrast to the 9 other lanthanides from praseodymium to thulium), *Urbain* [8] showed in 1905 that a group of very narrow bands start in the ultra-violet at 32200 cm^{-1} (311 nm). In the aqua ion, the strongest transitions [9] occurring between 35930 and 36710 cm^{-1} go to the six J-levels of ^6I, whereas the lowest level is $^6P_{7/2}$ (described to a good approximation by the quantum numbers appropriate for the spherical symmetry of monatomic entities $S = 5/2$, $L = 1$ and $J = 7/2$) and most frequently *fluorescent*. It is known from the Sm(III), Eu(III), Tb(III) and Dy(III) aqua ions [10–12] that the life-time of their fluorescent level in the visible increases by a factor 26, 54, 12 and 18, respectively, when going to deuterium oxide from ordinary water. This exemplifies the much stronger non-radiative desexcitation due to O–H stretching frequencies, which are $\sqrt{2}$ times those of O–D. There is a general exponential decrease of the probability of non-radiative decay as a function of the number of phonons (vibrational quanta) bridging the excited state and the groundstate [13]. *Haas* and

Stein [14] found a fluorescent quantum yield only 1.7 times higher of Gd(III) in D_2O than in H_2O showing that the observed half-life (close to 2 msec) is not much below the radiative half-life according to *Einstein*'s formula from 1917. Accordingly, many vitreous materials [13,15] show intense narrow-band fluorescence from $^6P_{7/2}$ and it is conceivable [15,16] that *four-level lasers* can be constructed, based on the anti-ferromagnetic coupling of Gd(III) through bridging oxide anions to other paramagnetic species (with positive S) or on simultaneous excitation (to the extent to 10000 cm^{-1}) of Yb(III), the other element discovered by Marignac.

The groundstate (with $S = J = 7/2$ and L zero) is situated 168 $D/13$ below the barycentre of the 3432 states (forming 327 J-levels) of the electron configuration [54] $4f^7$. Here, D is the parameter of *spin-pairing energy* [17,18] and the groundstate is about 85000 cm^{-1} (or 10.5 eV) below this barycentre. It seems that the small irregularities of complex formation constants (as a function of Z) at Gd(III) can be ascribed [19,20] to D being a few tenths of a percent smaller (due to the nephelauxetic effect [17]) in complexes compared with the less covalent aqua ions. The "ligand field" effects acting on the $(2J + 1)$ states of a given J-level are far too weak to provide an explanation.

The 8 states of the lowest J-level can, at most, separate into 4 *Kramers* doublets. Since the *Pauli*-self-conjugate half-filled 4f shell has very severe constraints on the "ligand field" splitting [21,22], their total spreading of energy is only 0.2 to 2 cm^{-1} and not the hundred times higher values characterizing the other trivalent lanthanides. A corollary is that very fine details of the *electron paramagnetic resonance spectrum* can be studied, including the tiny decrease of the gyromagnetic factor g from the *Schwinger* value 2.0023. It is possible to detect the sharp lines in spin resonance spectra of very low concentrations of Gd(III) and investigate their differing sites, e.g. in fluorite-type crystals [23–25] including adjacent defects. The results for Gd(III) in anti-fluorite Na_2S [26] and in the tetragonal [27] crystals MFX (where M = calcium, strontium, barium or lead, and X = chlorine or bromine) show unexpected effects of chemical bonding, which are quite incompatible with an electrostatic "ligand field" model. This situation is extreme, when gadolinium is incorporated in palladium [28,29], in gold [30] and in rhodium-palladium and palladium-silver alloys [31] as well as in the cubic crystals of the stoichiometric alloy $LaAl_2$ [32]. Paramagnetic resonance has also been detected of $4f^{11}$ erbium(III) in palladium [33]. Such measurements are of interest for studying local magnetic fields and superconducting metals. This is particularly true for the superconducting *Chevrel* phases such as $Ln_xMo_6S_8$ and $Ln_xPb_{1-x}Mo_6S_8$ [34–37]. Recently, new results were obtained for gadolinium in platinum [38]. The subject of electron spin resonance of lanthanides in metallic samples has been reviewed [39,40].

The *Curie-Langevin* paramagnetic behaviour of Gd(III) salts has technological importance for *cryogenics* in the millikelvin range, where a sample such as $Gd_2(SO_4)_3$, $8H_2O$ [41] is cooled in a strong magnetic field with liquid helium, the thermal contact interrupted, and the magnetic field turned off, with the result that nearly all the remaining heat content is used to disorder the magnetic moments and increase the entropy. This technique has made it possible [42] to study the many fascinating properties of liquid helium 3 and 4, obeying *Fermi-Dirac* and *Bose-Einstein* statistics, respectively. One of the most remarkable properties of metallic gadolinium is that it is *ferromagnetic* up to a Curie temperature 293 K (just at room temperature). This is much lower than nickel, cobalt and iron, but higher than of terbium (220 K) and of dysprosium and other lanthanides. Non-metallic gadolinium compounds all contain Gd(III), it can be deduced from the spin-pairing energy theory [17,18,43,44] that neither Gd(II) nor Gd(IV) would be feasible. Stoichiometric metallic compounds such as the CsCl-type GdZn and GdMg, the NaCl-type GdS, or GdI_2 or Gd_2Cl_3 have magnetic properties indicating Gd(III) whereas the conduction electrons may perhaps have pronounced 5d or 6s character. The I^* (ionization energies relative to the Fermi level) measured by *photo-electron spectra* [45,46] correspond to ionization forming the lowest term ^7F of $4f^6$ and are 8.0 eV the metallic element, 9.1 eV for GdSb and 8.9 eV in GdS (to be compared with 2.0 eV for Sb5p and 4 eV for S3p) whereas I relative to vacuo all are about 3 eV higher. I' (corrected for charge-compensating effects) is 14.1 eV for Gd_2O_3 and 15.5 eV for GdF_3. Not only are these ionization energies much higher than of the conduction electrons in the metallic samples, but also of $4f^7$ compared with the loosest bound orbitals of the other atoms in the compounds. This creates a certain paradox [46–48] in the description of weakly covalent bonding, where the important parameter is (the much lower) electron affinity of the partly filled shell. As first shown by comparison [49] of EuS with GdS, the isoelectronic Eu(II) have $I(4f)$ some 7 eV lower than Gd(III) under equal circumstances, and Tb(IV) in oxides 10 eV higher than Gd(III). This is the major reason [18,44] for an almost invariant oxidation state in the lanthanides. Whereas the photo-electron spectrum of Gd(III) shows only one 4f signal, the ionization $4f^8 \rightarrow 4f^7$ of Tb(III) corresponds to four signals due to formation of ^8S, ^6I, ^6G and ^6H [45,46,50] and comparison with the known terms [9] of Gd(III) and the expected increase (20 percent) of the term distances from Gd^{+3} to Tb^{+4} allows the surprisingly high nephelauxetic ratio $\beta = 0.93$ to be evaluated [18,46] for metallic terbium and TbSb. Unfortunately, the *atomic spectrum* of gaseous Gd^{+3} is only known in a very fragmentary way. However,

there is little doubt that β of the Gd(III) aqua ion is somewhere between 0.98 and 0.99. The groundstate of the gaseous gadolinium atom $^9D_2$ belongs to [54] $4f^75d6s^2$ and not (like 11 among the neutral lanthanide atoms) to [54] $4f^q6s^2$. This atom [51] has the rather unique property of showing well-characterized terms with $S = 5$, such as even ^{11}F, ^{11}D and ^{11}P belonging to [54] $4f^75d6s6p$ and odd ^{11}F and ^{11}P belonging to [54] $4f^75d^26s$. The general tendency of the lanthanides to provide high values of S and J has been further discussed [52,53].

It is clear that the individual lanthanides differ mainly in their spectroscopic and other physical properties. Though gadolinium was discovered by Marignac at a time when a weak and smooth variation of the chemical properties was thought to be the main characteristic of the rare earths, this element has continued to attract interest in the University of Geneva. The magnetic properties continue to be intensively studied both at Départment de Chimie physique and at Département de Physique de la Matière condensée. The luminescence and energy transfer are investigated with our invited Professor *Renata Reisfeld*, and the writer is invited to give a talk in the session on Solid State Laser Materials (chairman: Professor *R.C.Powell*, Oklahoma State University) on "Optimized Four-level Lasers" at the International Laser Conference in New Orleans in December 1980. Finally, in continuation of their work [54,55] on time-resolved luminescence spectra of the uranyl ion in aqueous solution, Professor *Marcantonatos* and his collaborators attempt to detect narrow transitions to higher sextet levels of the Gd(III) aqua ion, suddenly brought into its first excited state by a flash.

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