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Bicentenary of Four Platinum Group Metals

PART II: OSMIUM AND IRIDIUM – EVENTS SURROUNDING THEIR DISCOVERIES

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This paper follows an earlier one on the discoveries of rhodium and palladium in 1803 by William Hyde Wollaston (1). In 1804, two more of the platinum metals: iridium and osmium were discovered, also in London. This paper concerns the bicentenary of their discovery by Wollaston's friend and collaborator, Smithson Tennant.

In Part I, the brilliant work of William Hyde Wollaston on the isolation of rhodium and palladium was described (1). Here, the lesser-known figure of Smithson Tennant and his isolation of the much more intractable elements iridium and osmium is considered. This bicentennial work of 1804, reported by Tennant two years after Charles Hatchett's discovery of niobium (2), was an endeavour in which he was pursued by his French contemporaries H. V. Collet-Descotils, A. F. de Fourcroy and L. N. Vauquelin. Tennant was a less flamboyant but no less interesting person than his friend Wollaston, and undoubtedly he was as original and creative a chemist, but he was lacking in drive and was nowhere near as productive.

Although there is no full-scale biography of Tennant, there is an invaluable memoir by his friend, the lawyer John Whishaw, written anonymously in the *Annals of Philosophy* in 1815 (3). This was published, with very minor changes, as a booklet in the same year (4). Subsequent nineteenth century accounts, by Thomas Thomson in 1830 (5) and by Sir John Barrow in 1849 (6), rely heavily on these, as do more modern accounts (7–10).

In 1854 Henry Gunning ('Senior Esquire Bedell for Christ's College, Cambridge') reported some interesting anecdotes (11), and in 1940 A. E. Wales wrote a thesis (unpublished) with a brief but useful published summary (7). In 1961, this Journal commemorated the bicentenary of Tennant's birth (12).

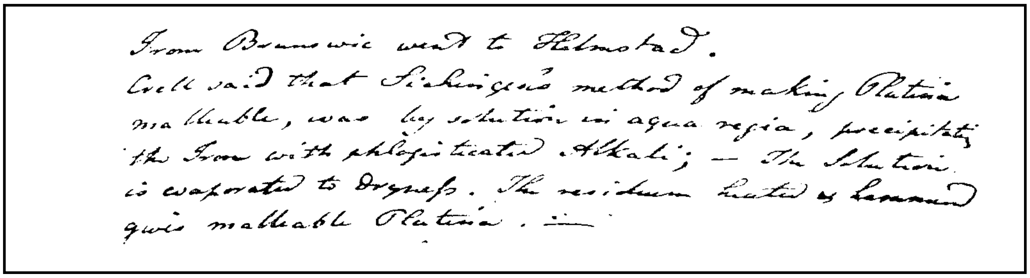
Smithson Tennant: Early Years

Tennant, a clergyman's son, was born on 30th November, 1761, at Finkle Street, Selby, Yorkshire. The origin of his unusual Christian name (Smithson) is not clear – possibly it derived from the surname of an earlier family member. His father died when he was ten, and his mother died in a horse-riding accident when he was twenty. (In 1815 Tennant was to lose his life in a rather similar accident.) He showed an early interest in chemistry, making gunpowder for fireworks when he was nine years old (3). In 1781 he studied medicine at Edinburgh University, attending lectures by Joseph Black, and in 1782 he joined Christ's College, Cambridge, studying chemistry and botany. In this year too he received an inheritance of lands in and near Selby and probably some land in Wensleydale from his deceased parents, and these are likely to have provided him with an income for life (9).

In 1784, aged 23, he travelled to Denmark and Sweden, where he met Carl Scheele and the mineralogist Johann Gahn, and by 1785 he had taken up an unfashionable antiphlogistic view of chemistry (3, 4). In 1786 he travelled to France and Holland; in France he met Berthollet and may well have met Lavoisier (7). In the same year he went to Emmanuel College, Cambridge, and graduated as M.D. in 1796, although he seems never to have practised medicine. He met William Wollaston (1) at Cambridge, and after he moved to London they became lifelong friends and collaborators.

Fellow of the Royal Society

On 13th January, 1785, at the extraordinarily young age of 24, he was elected a Fellow of the Royal Society, despite not yet having scientific publications. Much later, in November 1804, he was awarded the Royal Society's Copley medal,


From Brunswic went to Helmstad.
Crell said that Sickingen's method of making Platina
malleable, was by solution in aqua regia, precipitating
the Iron with phlogisticated Alkali; — The Solution
is evaporated to Dryness. The residuum heated & hammered
gives malleable Platina.

Smithson Tennant became interested in native platinum while still a student at Cambridge. This is an extract from his diary for October 4th 1784, when has was only twenty two, and describes his visit to Lorenz Crell at Helmstädt. It records the details of Count von Sickingen's method of rendering platinum malleable

mainly for the discovery of osmium and iridium.

Around 1793 Smithson Tennant took up residence at No. 4, Garden Court in the Temple, quite close to Somerset House the then home of the Royal Society, and here he remained until his death. In December 1800 he entered into a formal partnership with Wollaston for the purchase of a large quantity of platinum ore (1, 10) with which he was to do his osmium and iridium work. In 1812 the great Swedish chemist Berzelius visited him at his farm in Somerset, and in May 1813 he became the eighth Professor of Chemistry at Cambridge in the so-called '1702' chair. There, in April and May 1814 he delivered his one and only course of lectures, on the history and principles of chemistry, to a large and enthusiastic audience which included Charles Babbage and John Herschel (7).

Tennant had given up horse riding after his mother's fatal accident in 1781, but some fifteen years later he was advised to take it up again to improve his health, and thereafter rode daily, despite having a serious accident in 1809. On 22nd February, 1815 he rode over a wooden bridge near Boulogne, but the bolt securing the bridge was weak. It snapped and the bridge collapsed. Tennant was thrown from his horse, which fell on top of him into the deep ditch beneath, and he died an hour later from a fractured skull.

Tennant's Chemical Work

Tennant published very few papers, though on a variety of topics. The most striking, apart from the topic of this paper, was his demonstration in 1797 that diamond and graphite are both allotropes of carbon. He showed that the combustion of diamond, by heating with saltpetre in a gold tube, gave only carbon dioxide – this he measured gravimetrically by the amount of calcium carbonate formed from lime water. He found that the amount formed was the same as that shown earlier by Lavoisier who had oxidised a similar quantity of charcoal. On one occasion, he was involved in a combustion of diamond when the time for his ride came, so he abandoned his experiment (and presumably the burning diamond) and rode away (5).

Tennant's other published work includes papers on the composition of carbon dioxide in 1791, the formation of calcium phosphate, a development of the technique of double distillation, the nature of boric acid, emery, magnesia, dolomite and marble. Tennant developed a new method for making potassium metal, worked on the corrosion of gold and platinum by fusion with nitre, and studied the unsatisfactory effects of magnesian limestone as a fertiliser.

Personal Accounts of Tennant

Unfortunately there is no portrait of Tennant extant and indeed there seems never to have been one. Whishaw (3, 4) noted this and wrote that:

> *'Mr. Tennant was tall and slender in person, with a thin face and light complexion. His appearance, notwithstanding some singularity of manners, and great negligence of dress, was on the whole striking and agreeable. The general cast of his features was expressive, and bore strong marks of intelligence; and several persons have been struck with a general resemblance in his countenance to the well-known portraits of [John] Locke.'*

Although Wishaw's account is largely a panegyric it does include some slightly critical comments, specifically his extreme untidiness:

'His……rooms exhibited a strange, disorderly appearance of books, papers and implements of chemistry, piled in heaps and thrown in confusion together' (3, 4).

Henry Gunning mentions that:

'when at a loss for a piece of linen to filter some of his preparations he never scrupled taking a part of a cambric handkerchief for the purpose, or cutting off a piece of shirt' (11).

Thomson, writing some years after Tennant's death, refers to his

'uncommon chemical skills.....the powers of his mind...were of the highest order.'

He then goes on to say that:

'his farming speculations, as might have been anticipated from the indolent and careless habits of Mr. Tennant, were not very successful' (5).

The word indolent appears in a number of accounts of Tennant (3–5, 7, 10), and even in Sir Joseph Banks' speech at the Royal Society congratulating him in 1804 on the award of the Copley medal (an event at which Tennant surprisingly – but perhaps typically – was not present) he exhorted Tennant to greater efforts in his chemistry (10). Nevertheless, all attested to his passion for music, theatre, literature (and civil liberties). He remained, like Wollaston, a bachelor throughout his life.

Tennant's Work on Osmium and Iridium

It was described in Part I (1) how Wollaston and Tennant divided the work of isolating the elements osmium and iridium from crude alluvial platinum ore. Wollaston worked on the portions soluble in *aqua regia* while Tennant had the less enviable task of investigating the insoluble residues. However he had considerable quantities of material with which to work – some 100 ounces Troy of the black powder (10) – a luxuriously large quantity which his French rivals certainly could not

XVI. *On two Metals, found in the black Powder remaining after the Solution of Platina. By* Smithson Tennant, *Esq. F. R. S.*

Read June 21, 1804.

UPON making some experiments, last summer, on the black powder which remains after the solution of platina, I observed that it did not, as was generally believed, consist chiefly of plumbago, but contained some unknown metallic ingredients. Intending to repeat my experiments with more attention during the winter, I mentioned the result of them to Sir JOSEPH BANKS, together with my intention of communicating to the Royal Society, my examination of this substance, as soon as it should appear in any degree satisfactory. Two memoirs were afterwards published in France, on the same subject; one of them by M. DESCOTILS, and the other by Messrs. VAUQUELIN and FOURCROY. M. DESCOTILS chiefly directs his attention to the effects produced by this substance on the solutions of platina. He remarks, that a small portion of it is always taken up by nitro-muriatic acid, during its action on platina; and, principally from the observations he is thence enabled to make, he infers, that it contains a new metal, which, among other properties, has that of giving a deep red colour to the precipitates of platina.

M. VAUQUELIN attempted a more direct analysis of the substance, and obtained from it the same metal as that discovered by M. DESCOTILS. But neither of these chemists have observed,

During Wollaston's researches into the purification of platinum by dissolution of native platinum ore in aqua regia, a large amount of insoluble black powder remained as a byproduct of this operation. While Wollaston concentrated on the soluble portion, Tennant examined the insoluble residue. In the summer of 1803, Tennant identified two new elements, iridium and osmium. This was documented in the paper he read to the Royal Society in 1804 (31)

have had. It seems that Wollaston worked rather harder than Tennant on some of their joint platinum research, but the latter carried out all the osmium and iridium work, possibly with Wollaston's constant urging. He was fortunate, or well-advised enough (perhaps by Wollaston), to publish his work speedily – because the French rivals were hotly in pursuit; indeed, he privately communicated his results to Sir Joseph Banks, his and Wollaston's mutual friend and at that time President of the Royal Society, prior to its publication. His paper was read to the Royal Society on June 21st, 1804 (13).

Discovery of Osmium

Tennant first showed that the black residue obtained after heating crude platina in *aqua regia* had a density of 10.7, far too great for the earlier (14) suggestion that it was plumbago (graphite).

Tennant heated the black powder remaining from the *aqua regia* treatment of crude alluvial platina with sodium hydroxide to red heat, cooled the melt and dissolved the resulting mass in water. The yellow solution thus obtained, which probably contained *cis*-$[Os(OH)_2O_4]^{2-}$ as well as OsO_4, had a very pungent smell. On acidification the solution gave a white volatile oxide, undoubtedly osmium tetroxide, OsO_4, which was distilled off and studied (he subsequently made it more directly by fusing the black powder with nitre, KNO_3).

Of this oxide he wrote:

> *'it stains the skin of a dark colour which can not be effaced.................(it has) a pungent and penetrating smell....from the extrication of a very volatile metal oxide....this smell is one of its most distinguishing characters, I should on that account incline to call the metal Osmium'.*

The name is derived from the Greek οσμη – osme, smell. He reduced an aqueous solution of the oxide to black osmium metal by treatment with copper, silver or zinc (13).

Sowerby, in his 'Exotic Mineralogy' of 1811, illustrated some samples collected by Wollaston of *Iridium Osmiferrum*, which we would now call osmiridium, collected from 'Peruvian Platina' (15).

Discovery of Iridium

As with his osmium work Tennant heated the black powder he obtained from treating crude platina with *aqua regia* in a silver crucible. This was followed by fusion with caustic soda at red heat. The resulting cooled mass was then dissolved in water, and the black residue remaining was treated in "marine acid" (hydrochloric acid). The residue was again fused with caustic soda and extracted with HCl, giving dark red crystals, probably of $Na_2[IrCl_6].nH_2O$. On heating these an unknown element was obtained as a white powder which

> *'appeared of a white colour, and was not capable of being melted, by any degree of heat I could apply..........I should incline to call this metal Iridium, from the striking variety of colours which it gives, while dissolving in marine acid.......'* (13).

Iridium is named after the Latin *iris*, a rainbow.

Parallel Work on Osmium and Iridium by French Chemists

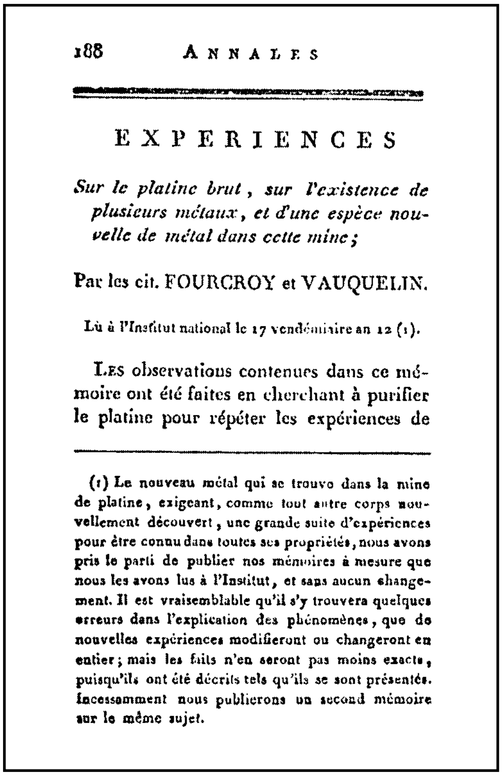
In 1801 Proust had studied the dissolution of crude platina in *aqua regia* and attributed the small amount of black residue remaining to 'nothing else but graphite or plumbago' (14), a claim dismissed by Tennant, as already noted. Antoine François de Fourcroy (1755–1809), a chemist of profound knowledge and insight (16), was working with Nicolas Louis Vauquelin (1763–1829), a very gifted experimentalist (17), on the problem of this black residue. Vauquelin's interest in this topic may well have been aroused by the examination he had made of the palladium sent to him for analysis by Wollaston (1, 18).

In September and October 1803 Fourcroy and Vauquelin read a paper to the Institut Nationale de France in Paris, published in 1804, in which they described their study of this black solid. They fused it with potash, extracted the cooled melt with water (to give a solution which they believed contained chromium but which may also have contained rhodium – later to be isolated by Wollaston in 1804 (19)) and treated the residue with more *aqua regia*. Addition of ammonium chloride to the latter gave, depending on conditions, red or yellow crystals. They thought that the red crystals contained a compound of a new metal, in addition to compounds of titanium, chromium, iron and copper.

These crystals could well have been, or could have contained, iridium as $(NH_4)_2[IrCl_6]$, but crucially they did not name their "new element" (20).

It is interesting to note that the references (18, 20 and 22) are to Cit. (citoyens) Fourcroy and Vauquelin, with no initials: this was common practice in French journals in early Revolutionary times.

On the same day as their first memoir was read to the Institut in September 1803, Hippolyte Victor Collet-Descotils (1773–1815), who had been a student of Vauquelin, reported essentially similar results, and published a more concise paper in 1803 (21). Like the cautious Fourcroy and Vauquelin he did not name the new metal which he believed to be present, but said that he would assign it a name after further research. In February


188 ANNALES

EXPERIENCES

Sur le platine brut, sur l'existence de plusieurs métaux, et d'une espèce nouvelle de métal dans cette mine;

Par les cit. FOURCROY et VAUQUELIN.

Lû à l'Institut national le 17 vendémiaire an 12 (1).

Les observations contenues dans ce mémoire ont été faites en cherchant à purifier le platine pour répéter les expériences de

(1) Le nouveau métal qui se trouve dans la mine de platine, exigeant, comme tout autre corps nouvellement découvert, une grande suite d'expériences pour être connu dans toutes ses propriétés, nous avons pris le parti de publier nos mémoires à mesure que nous les avons lus à l'Institut, et sans aucun changement. Il est vraisemblable qu'il s'y trouvera quelques erreurs dans l'explication des phénomènes, que de nouvelles expériences modifieront ou changeront en entier; mais les faits n'en seront pas moins exacts, puisqu'ils ont été décrits tels qu'ils se sont présentés. Incessamment nous publierons un second mémoire sur le même sujet.

*The opening page of the first memoir on the analysis of crude platinum by Fourcroy and Vanquelin (Anales de Chimie, 1804, **49**, p. 188) (17)*

1804 Fourcroy and Vauquelin announced further experiments on the black residue (this work is unlikely, in view of the dates, to have been known to Tennant). They found that fusion with potash and extraction with water lead to a solution which had a strong smell affecting the eyes and throat (*une action très-fort sur les yeux et sur le gosier*); on distillation the vapour blackened skin and cloth. They mistakenly thought this to be a volatile oxide of the un-named metal they had observed earlier, but it is clear in retrospect that they had made osmium tetroxide (22).

Although it is clear from Tennant's paper (13) that he knew of the early work of Fourcroy and Vauquelin (probably at least some of that described in (20)), he would not have known of their later experiments and does not mention the work of Collet-Descotils. In 1806 Fourcroy and Vauquelin magnanimously admitted that Tennant's work had been superior to theirs (23), and Vauquelin in 1814 attributes the discovery of iridium and osmium to Tennant, suggesting that the black powder also contains titanium, iron, silicon and aluminium (24).

Osmium and Iridium in the Nineteenth Century

There are references in the literature (8, 25, 26) to *ptene* or *ptène* (from the Greek πτηοζ *ptenos*, winged) as a name for osmium; indeed, Tennant is said to have proposed this name for it (8, 25), whereas Partington (26) says that Fourcroy and Vauquelin proposed it (20, 21). The author can find no trace of this ungainly name either in Tennant's paper (13) or in those of the French authors. The symbol proposed by Berzelius was the familiar Os, and for iridium he proposed first I, later changing it to Ir (27).

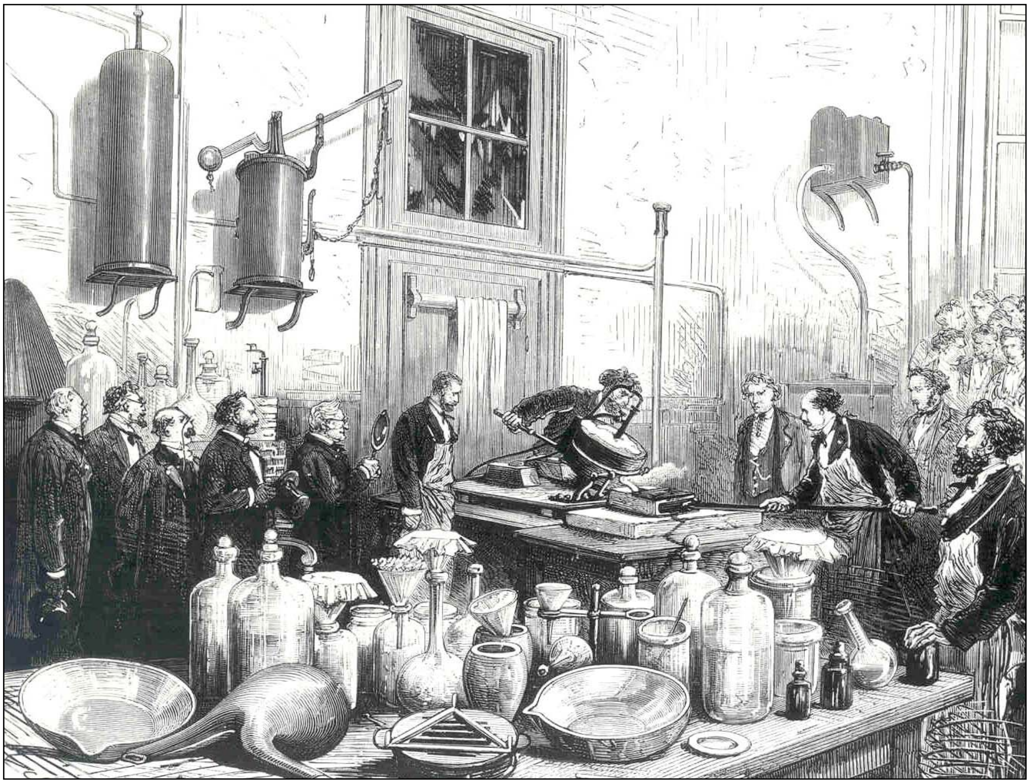
In his penultimate paper, read as the Bakerian Lecture to the Royal Society on 20th November 1828, a month before his death, Wollaston described the preparation of malleable platinum and palladium and also described his method of making pure osmium tetroxide. He fused osmiridium in alkali to red heat, extracted the cooled melt with water and treated the filtrate with sulfuric acid, distilling out pure osmium tetroxide (28).

In 1828 Berzelius studied the compounds of osmium and tried to determine its atomic weight (29). He then studied iridium similarly (30).

Initial Uses of the Metals

Some industrial uses for the metals were found in the nineteenth century. The manufacture of two rhodium-iridium-silver-steel razors, which were presented to Michael Faraday, was mentioned in Part I (1). The use of osmium tetroxide for biological tissue fixation (that is the preservation of tissue and its delineation for optical and electron microscopy) dates back to the middle of the nineteenth century and continues to this day.

In 1874 massive amounts of platinum-iridium alloy were used as standard metre lengths but it transpired that these contained some iron and ruthenium impurities. These problems were overcome and for many years standard metres and standard kilogrammes made of Pt-Ir alloy were



In 1873, the President of France, Louis Adolphe Thiers, together with a number of his ministers, observed the melting of ten kilograms of iridium-platinum for the production of the new standard metre, in Deville's laboratory in the École Normale. Deville is standing in front of the door looking thoughtful, and the President is holding a protective glass in front of his eyes

kept in Paris (31). Platinum-iridium alloys were also used in 1862 as boiling vessels for the concentration of sulfuric acid. In 1879 Thomas Edison experimented with platinum, iridium-platinum and pure iridium filaments for incandescent light bulbs, and Carl von Welsbach used osmium filaments in 1897.

In the late nineteenth century work was carried out on the use of iridium and of iridium-platinum alloys for thermocouple and temperature measurement purposes (31). Fritz Haber initially used osmium just after the turn of the century as a catalyst for the production of ammonia from nitrogen and hydrogen, but later used a much cheaper iron-iron oxide catalyst; and in 1918 he received the Nobel Prize in Chemistry for this work (32).

Sir William Crookes persuaded Johnson, Matthey to "fashion" crucibles of rhodium, iridium, ruthenium and osmium; if they succeeded with the latter two metals Crookes does not record, but he found iridium to be "*as hard as steel and….unaffected by any mechanical treatment that can reasonably be applied to it*". He found it to be resistant to attack by any chemical except caustic potash at red heat, and even in these conditions it had greater resistance than platinum (33). The use of iridium or iridium-platinum crucibles continues to this day and constitutes a valuable application for the metal.

The Densities of the Metals

For many years it has been known that osmium and iridium have the highest densities of any known metals, but which is the heavier of the two has been a hotly contested issue.

It is now clear that osmium (density 22.587 $\pm$ 0.009 g cm^{-3}) is very slightly denser than iridium (22.562 $\pm$ 0.009 g cm^{-3}) (34).

Conclusions

These two papers have celebrated the bicentenaries of the discovery in London of four of the six platinum group metals, by William Hyde Wollaston and Smithson Tennant. All four elements have important industrial and in particular catalytic uses. (In 2001, rhodium and osmium were cited in the Nobel Prize awarded to Knowles, Noyori and Sharpless (35)). They possess rich and varied chemistry, are extensively used in scientific research, and constitute and provide fertile ground for new discoveries and technologies.

Appendix: Residences and Memorials of Tennant

Tennant was born in Finkle Street, in the centre of Selby, near the Abbey church where he was baptised. The building (probably No. 12, now a public house) still stands.

After Cambridge Tennant moved to London and stayed at No. 4, Garden Court, Temple (adjacent to the Middle Temple on its south-west side) where he carried out his osmium and iridium work. Buildings on the site are still there, renumbered 1 and 2 Garden Court; No. 4 was demolished in 1884 but the present Nos. 1 and 2 probably occupy the same site (36). Tennant may have had rooms there.

The ground floor was occupied by the collections of the Geological Society, which was formed in 1807 and moved at least some of its mineralogical collections to 4 Garden Court. Tennant was a Vice-President and Council member of the Geological Society from 1813 to 1815 (36). There was a pub close by, the Crown and Anchor Tavern in Arundel Street near the Strand: sadly it has been demolished, but was the site of an informal dining and conversation club for some members of the Royal Society called the King of Clubs. This was frequented by Davy, Wollaston and, during his trips to London, Dalton and others. It seems highly likely that Tennant, a sociable person who lived close by, also attended. He purchased seven acres of farmland near Epworth, Lincolnshire, in 1799, and in the same year bought some five hundred acres at Shipham, in Somerset. The land was principally used for his experiments on fertilisers rather than for agriculture. He built a house on the Shipham land and used this as a summer residence (7, 10). This still stands, albeit with some additions, as Longbotton Farm. In his birth place, Selby, a residential road on the outskirts of the town is named Tennant Street in commemoration of him.

Tennant is buried in the public cemetery in Boulogne, with a Latin inscription on the headstone. He left no will (9). No pictures or sketches of Tennant survive, indeed it is believed that none was ever made (3, 4).

Bibliographies

The very comprehensive bibliographies by J. L. Howe covering the period 1748 to 1950 are indispensable for the early work (37). The author wrote a survey of the chemistry of iridium and osmium, covering the literature up to 1967 (38) and on the non-organometallic chemistry of osmium (39), osmium tetroxide (40) and iridium (41). More up-to-date, though less comprehensive, is a book on the six platinum group metals by Cotton (42). The "Encyclopedia of Inorganic Chemistry" has useful articles on the coordination and organometallic chemistry of iridium (43) and osmium (44).

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