The chemistry of palladium, platinum and rhodium ‘nitrates’.

Introduction

In the early 1960’s Ralph Pearson developed a set of Rules for hard/soft Lewis acids and bases. [1,2] The platinum group metals are soft metals and prefer to coordinate to soft ligands; for example, cyanide, ammonia, amines, sulphur ligands and halides etc. They do not easily form complexes with hard ligands, such as oxo acids (nitrate, sulphate, phosphate etc). Platinum group metals therefore do not form ‘simple’ nitrate compounds. What follows is a description of the chemistry of the ‘platinum group metal nitrates’ that are placed on the market. It is based exclusively on public domain information, but is known to be consistent with Industry generated data, which is considered to be commercially sensitive.

The chemistry of ‘palladium (II) nitrate’

Although it is placed on the market as palladium (II) nitrate, it is very unlikely that the substance contains any of the simple nominal nitrate substance.

‘Palladium (II) nitrate’ is often produced by for example, the dissolution of palladium metal or palladium (II) hydroxide/hydrated oxide in nitric acid. Various authors have claimed that the product of dissolving palladium powder in nitric acid is Palladium (II) nitrate or $[Pd(NO_3)(OH_2)_2]$. [3,4] Gatehouse et al [5] confirmed that the species contained coordinated unidentate nitrato ligands. In addition to nitrato species, the formation of nitrito species in nitric acid solutions is well known [6].

Generally, the platinum group metals form series of complexes with say, chloride, nitrito or nitrato ligands (X) from the hexa aqua through to the hexa X complexes. In the case of palladium (II) they are tetra coordinate and are of the general formula $[Pd\ (X)_n\ (H_2O)_{4-n}]^{(2-n)}$. The proportions of the various members of these series generally vary with the concentration of X. There is also the possibility of mixed nitrato-nitrito-aqua palladium (II) complexes.

Because the exact proportions of any nitrato, nitrito and aqua ligands will vary with the method of production, concentration of nitric acid, treatment conditions and ageing (giving rise to re-equilibration), this ‘palladium (II) nitrate’ substance has been declared as a UVCB.

The chemistry of ‘platinum (II) nitrate’

Although this substance is placed on the market as ‘platinum (II) nitrate’ it is very unlikely that it contains any of the simple nominal nitrate substance.

The key paper here is considered to be that by Danan Dou et al [7]. One of the most striking features of which was that the authors used XANES and EXAFS to conclude that the species present are actually Platinum (IV). They proposed that the species are made from two ocatahedral platinum atoms linked by bridging oxo and/or hydroxyl moieties. This primary oligomer structure then gives rise to more complex polymer structures. At no point did the authors detect any ‘Pt nitrate’ containing species; although the detection limits of XAS techniques are sufficiently high that this should not eliminate the possibility of low levels of other species. In aqueous systems, platinum (IV) forms classical hexa coordinate series with unidentate soft ligands (X), which have the general formula $[Pt(X)_n(H_2O)_{6-n})]^{4-n}$. The proportions of the various members of these series generally vary with the concentration of X. Note that, in the oligomer, platinum is coordinated to oxo species, which are stabilised by the polymeric structures formed.

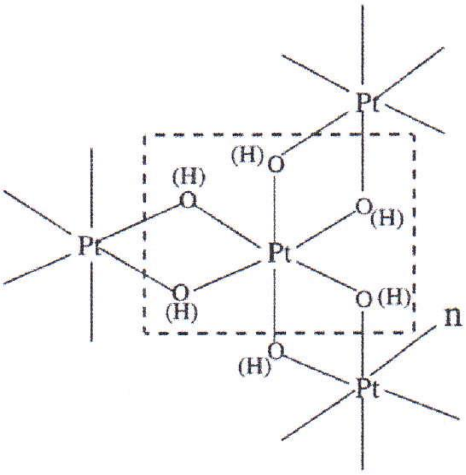

Figure 1: Pt oligomer, from Donan Dou et al [7]

This is consistent with Industry observations; as under some undefined conditions it is known that ‘platinum (II) nitrate’ solutions may form gels after a period of time, which can reasonably be assumed to be due to continuing polymerisation.

Because of the undefined polymeric nature of ‘platinum (II) nitrate’ and the possibility of minor amounts of other platinum nitrate species, the proportions of which are uncontrolled and may vary with production conditions and ageing, this substance has been declared as a UVCB.

The chemistry of ‘rhodium (III) nitrate’

Although this substance is placed on the market as ‘rhodium (III) nitrate’ is it very unlikely that it contains any of the simple nominal nitrate substance.

A key paper here is considered to be that by Caminiti et al [8]. The authors used X-ray diffraction and Raman spectroscopy to study solutions of the nominal substance. They concluded that the Rh(III) was present as octahedral species at least a proportion of which, in a similar way to ‘platinum (II) nitrate’, was present as bridged polymeric rhodium species. On this occasion the bridging moieties were nitrato ligands, and some more conventional members of the nitrato-aqua Rh (III) series of complexes were also present. In aqueous systems, rhodium (III) forms classical hexa coordinate series with unidentate soft ligands (X), which have the general formula $[Rh(X)_n(H_2O)_{6-n})]^{3-n}$. The proportions of the various members of these series generally vary with the concentration of X.

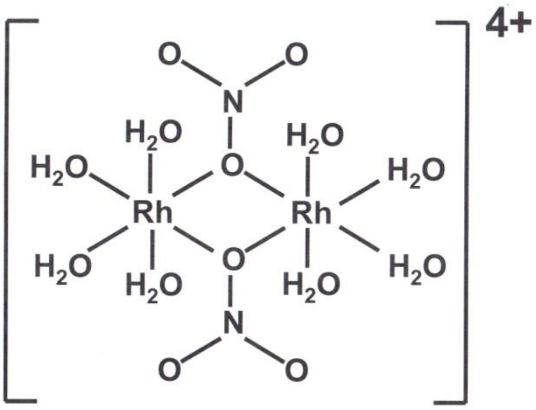

Figure 2 Nitrato bridged Rh species [8]

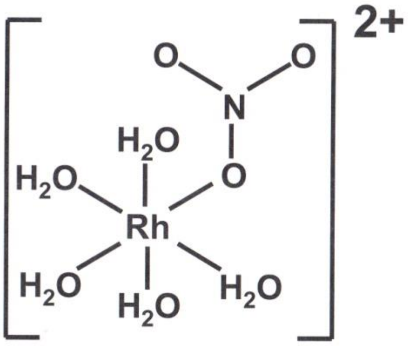

Figure 3 A conventional member of the hexa-coordinate Rhodium aqua-nitrato anation series[8]

This polymeric nature is partly supported by Belyaev et al [9] and Fedotov [10] who used nitrogen^{14}, oxygen^{17} and Rh^{103} nuclear magnetic resonance spectroscopy to propose a dimeric rhodium structure such as:

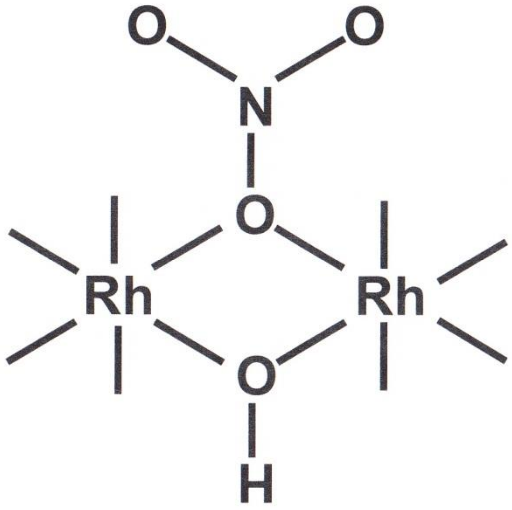

Figure 4 Nitrato, hydroxy bridged Rh species [9,10]

Note that, in this case, rhodium is coordinated to oxo species, which are stabilised by the polymeric structures formed.

Due to the variable ratios of undefined polymeric Rh (III) species and rhodium (III) mixed aqua nitrato complexes, the proportions and nature of which will vary depending on the production and storage conditions, this substance has been declared as a UVCB.

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References

1. Pearson R.G, Hard and Soft Acids and Bases, *JACS,* **85**, 3533-3539 (1963)
2. http://www.meta-synthesis.com/webbook/43_hsab/HSAB.html
3. Comprehensive Inorganic Chemistry, **3**, 1280, (1973)
4. A Comprehensive Treatise on Inorganic and Theoretical Chemistry, J W Mellor, **XV**, 684, (1947)
5. Gatehouse BM, Livingstone SE and Nyholm RS, *J Chem Soc*, 4222, (1957)
6. Tatarchuk VV et al, 'Formation of nitrite palladium complexes in nitric acid media.', *Zhurnal Neoorganicheskoi Khimii*, **47**(7), 1206-1210 (2002)
7. Danan Dou et al; Structure and chemical properties of Pt nitrate and application in three-way automotive emission catalysts , *Applied Catalysis B Environmental*, **30** 11-24, (2001)
8. Caminiti R, Atzel D, Cucca P, Anedda A and Bongiovanni G, Structure of Rhodium (III) Nitrate Aqueous Solutions' *J. Phys. Chem.,* **90**, 238-243, (1986)
9. Belyaev AV, Fedotov MA, Khraneko SP, Emel'yanov VA, *Russ J. Coord. Chem.* **27** (12), 855, (2001)
10. Fedotov MA, *Russ. J. Coord. Chem*. **28** (8), 575, (2002)