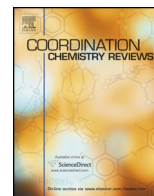




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### Review

# More of a misunderstanding than a real mismatch? Platinum and its affinity for aqua, hydroxido, and oxido ligands

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**Abbreviations:** 1,4-DACH, 1,4-diaminocyclohexane; 1MeC, 1-methylcytosine; 1MeC-N3, 1-methylcytosine coordinated through N3 site to metal; 1MeU, 1-methyluracil anion; 2,2':6',2''-trpy, terpyridine; 2,2'-bpy, 2,2'-bipyridine; 5'-GMP, 5'-guanosine monophosphate; BIAN, (N,N'-substituted) bis(imino)acenaphthene; COD, cyclooctadiene; CSD, Cambridge Structural Database; dien, diethylenetriamine; diphos, chelating diphosphane; DMSO, dimethylsulfoxide; EXAFS, Extended X-ray Absorption Fine Structure; gly-N, glycine bonded to metal through its amino group; HSAB, Hard and Soft Acids and Bases; PPh<sub>3</sub>, triphenylphosphane; py, pyridine; pz, pyrazolyl; SAXS, Small Angle X-ray Scattering; THF, tetrahydrofuran.

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Dedicated to Professor Henryk Kozłowski,  
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## ABSTRACT

This article reviews discrete complexes of platinum in its common oxidation states +II, +III, and +IV with aqua, hydroxido, oxido, and peroxido ligands, which at some point had been considered unstable and difficult to isolate because of an incompatibility between the “soft” nature of the metal and the “hard” nature of the O-ligands. The sheer number of structurally fully characterized examples contradicts this view, and numerous studies confirm their existence in solution and reveal at the same time distinct reactivity patterns. These make Pt complexes with O-donor atoms interesting candidates for medicinally important Pt antitumor drugs as well as catalytically relevant species.

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## 1. Introduction

It has been a simplified interpretation of the essence of the HSAB concept (HSAB = Hard and Soft Acids and Bases) [1,2] which has led to a widespread perception among coordination chemists that the “class b” or “soft” metal ion  $\text{Pt}^{2+}$ , and to a lesser extent even the “harder”  $\text{Pt}^{4+}$ , form only weak bonds with “hard” oxygen donor atoms, and moreover, that such complexes may be difficult to isolate. As we know today, this view has been erroneous. In fact, even decades before the implementation of the HSAB concept numerous reports on the existence of Pt complexes with O-donor ligands such as  $\text{OH}_2$ ,  $\text{OH}^-$ ,  $\text{ONO}_2^-$ , and  $\text{OSO}_3^{2-}$  had appeared [3–5], most of which eventually proved correct when X-ray crystallography became available decades later. By the 1960s the existence of complexes with Pt in +II and +IV oxidation states and O-donors such as oxalate, carbonate, or acetylacetonate, among others, was firmly established [6], and a whole new class of mixed-valence Pt compounds, based on bis(oxalato)platinate(II), had been described by K. Krogmann [7]. In fact, the latter dated back to work done by H.G. Söderbaum in 1886 already [8] and later by A. Werner [9]. Even a peroxide compound, with side-on bonded  $\text{O}_2^{2-}$ ,  $[\text{Pt}(\text{PPh}_3)_2\text{O}_2]$ , had been described [10,11]. In the late 1960s and early 1970s the existence of  $\text{Pt}^{\text{II}}\text{—OH}^-$  complexes with hydroxido ligands in terminal and bridging binding modes had been demonstrated [12–15]. Scientists in this field even then repeatedly had stressed the point that the predicted incompatibility between Pt and O-donors is questionable. Only considerably later was it shown that bonds between  $\text{Pt}^{\text{II}}$  and  $\text{MeO}^-$  or  $\text{OH}^-$  have the strengths of Pt–C bonds [16]. In retrospective the question may be asked whether the anticipated “mismatch” between Pt and O actually has been more of a “misunderstanding”. An attempt to rebalance some of the misunderstandings regarding the HSAB concept by developing “practical hardness-softness scales” has been undertaken, among others, by R.B. Martin for a selected series of metal ions and of ligands [17]. Based exclusively on experimentally determined stability constants valid for aqueous solutions, not *absolute* stability constants are compared, but rather *differences* in stability constants of a particular metal ion, in which one donor, e.g. a N-donor, is substituted by another one, e.g. a O-donor. Because of the lack of reliable stability constants for  $\text{Pt}^{\text{II}}$  complexes due to its slow kinetics to attain equilibrium, values for  $\text{Pd}^{\text{II}}$  can be taken as models of the former. According to such an analysis,  $\log K$  values for  $\text{Pt}^{\text{II}}\text{—OH}$  species are higher by 3.4 units than that of related  $\text{Pd}^{\text{II}}\text{—NH}_3$  compounds, for example!

While it is undisputed that S-donors, and in particular  $\text{HS}^-$  and  $\text{S}^{2-}$ , have a high affinity for  $\text{Pt}^{\text{II}}$ , exceeding that of O-donors by far, for other S-donors this is not always true. In  $[\text{Pt}(\text{DMSO})_4]^{2+}$  two ligands are bonded through the sulfur atoms, whereas the

two other DMSO molecules are bound via their oxygen atoms [18]. Regarding catalysis aspects, thermodynamically less stable bonds, viz. between Pt and O, are in fact advantageous!

As far as the aqueous solution chemistry of Pt complexes is concerned (see Section 2.1), the hydrolysis of ligands, hence the formation of Pt-aqua and subsequently hydroxido complexes, is responsible for the acidic behavior of these solutions and for much of its subsequent coordination chemistry:  $[\text{PtL}_n\text{X}] + \text{H}_2\text{O} \rightarrow [\text{PtL}_n(\text{OH}_2)] + \text{X}$  and  $[\text{PtL}_n(\text{OH}_2)] \rightarrow [\text{PtL}_n(\text{OH})]^- + \text{H}^+$ .

The extent of acidification of the aqua ligand bonded to Pt is dictated by a combination of different parameters (see Section 2.1). Interest in the solution chemistry of Pt complexes in water has been markedly spurred in the aftermath of the discovery of B. Rosenberg that *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (Cisplatin) is a potent anticancer agent [19]. It has been realized that in water, and similarly in the cytoplasm of a cell with its low concentration of chloride, successive replacement of the two chlorido ligands by water molecules takes place, which can form also hydroxido complexes, depending on pH, and even larger condensation products if concentrations are higher. In essence, a complicated mixture of hydrolysis products can exist, which can act differently with biological targets and may display differential toxicities (see Sections 3.4 and 3.6).

In this review we will focus largely on discrete Pt complexes with aqua, hydroxido, oxido, and peroxido ligands, and will mention the numerous other O ligands (e.g. inorganic or organic anions with coordinating O atoms, chelating ligands containing one or more or even exclusively O donors) only in passing or not at all. We will start out with structural and in particular X-ray structural aspects, before discussing selected reactivity patterns of complexes with these O-donors, with emphasis on the chemical biology of Pt-am(m)ine compounds. As far as X-ray structural reports on Pt complexes with O-donor ligands are concerned, until 1970 the number of examples was indeed small, with only 15 entries listed in ref. 6. By the late 1980s and early 1990s this number has increased moderately [20,21]. Today, as of February 2016, the Cambridge Structural Database (CSD) has more than 2500 entries on X-ray crystal structure analyses of Pt complexes containing O-donor atoms [22]. Regarding X-ray crystal structures of purely inorganic compounds, including complex salts with carbonate anions, as compiled in the Inorganic Crystal Structural Database (ICSD) [23] and the Scifinder Database [24], they boost this number further. A considerable part of relevant publications in the latter databases deals with mixed metal/platinum oxides (frequently termed metal “platinate”), with Pt oxides in +II and +IV oxidation states, as well as mixed-valence compounds and partially oxidized linear-chain bis(oxalato)platinate. They will be almost completely ignored in this text.



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