

# COMPLEXATION OF Pd BY NATURAL ORGANIC LIGANDS

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## Summary

Recently, the platinum-group elements (PGE) have become an environmental concern. Their use in automobile exhaust systems to reduce air pollution has resulted in their becoming contaminants in roadside dust and river sediments, sewage sludges, soils and the marine environment. It has been suggested that the PGE can be transported in aqueous environments in the form of complexes with natural organic ligands, but our understanding of such processes is very limited. Solubility and spectroscopic methods have been employed to study the interaction of Pd with the organic ligands acetate, oxalate, salicylate, phthalate and fulvic acid. The results show that all the organic ligands studied increase the solubility of Pd in aqueous solutions, and that this effect is indeed due to the formation of stable Pd(II)-organic ligand complexes. A preliminary estimate of the cumulative stability constant for the second Pd(II)-acetate complex of  $\log K = 9.2$  was determined. Speciation calculations suggest that oxalate can compete favorably with acetate, chloride and hydroxide ligands for Pd(II) in soil solutions. Acetate, oxalate, salicylate, and phthalate all bind to Pd(II) via oxygen-donor groups (carboxylate). Theoretical considerations suggest that N- and S-donor groups should form even stronger complexes with Pd(II), and experimental evidence suggests that amino acids do form very stable complexes with the PGE. It is likely that O-, N- and S-groups on natural fulvic acids are capable of solubilizing and transporting significant amounts of Pd in natural waters, particularly soil solutions and sediment porewaters.

## Introduction

In the past couple of decades, the PGE have been found to pose a significant environmental risk. Ironically, the use of these elements in automobile exhaust systems to reduce air pollution (among other uses) has resulted in their becoming contaminants in roadside dust and river sediments (Hodge and Stallard, 1986; Wei and Morrison, 1994), sewage sludges (Lottermoser, 1994), soils (Heinrich et al., 1996) and the marine environment (Lee, 1983; Esser and Turekian, 1993). The PGE may be both bioavailable and toxic under certain circumstances (Brubaker et al., 1975; Bunger et al., 1996; Gebel et al., 1997). The isotopes  $^{107}\text{Pd}$ ,  $^{103}\text{Ru}$  and  $^{106}\text{Rh}$  are fission products of nuclear fuel and the conditions of their potential migration from deeply buried nuclear waste repositories or contaminated surface sites into the biosphere must be understood (Brookins, 1986; McKinley et al., 1988). Knowledge of the stoichiometries and stability constants of potentially important PGE complexes is required to understand the mobility, bioavailability and biogeochemical cycling of these elements in the environment.

## Fundamentals of aqueous Pd chemistry

In natural aqueous solutions, the only important oxidation state of Pd is Pd(II) (Mountain and Wood, 1988). The aqueous ion ( $\text{Pd}^{2+}$ ) is a "soft" cation in the Pearson (1963) sense, and is predicted to form strong complexes with "soft" ligands such as  $\text{HS}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , and weaker complexes with O-donor

ligands and other "hard" ligands such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{F}^-$ . However,  $\text{Pd}^{2+}$  is one of the most strongly hydrolyzed ions (Baes and Mesmer, 1976); it forms very stable hydroxide complexes (van Middlesworth and Wood, 1999). With regard to complexes with organic ligands,  $\text{Pd}^{2+}$  should be expected to bind most strongly with ligands containing S- and N-donor groups, and less strongly with ligands containing only O-donor groups. However, it will be demonstrated below that ligands containing carboxylate form surprisingly strong complexes with  $\text{Pd}^{2+}$ .

## Importance of organic ligands

Several authors have suggested that organic ligands might be responsible for the behavior of PGE in aqueous surface environments (Cousins and Kinloch, 1976; Cousins and Vermaak, 1976; Dissanayake and Kritsotakis, 1984; Bowles, 1986; Wood and Vlassopoulos, 1990; Bowles et al., 1994, 1995). Humic substances (HS), such as humic and fulvic acids, may play particularly important roles in complexing PGE (cf. Wood, 1996). Acetate and oxalate are important simple carboxylic acid anions that occur naturally in soil solutions, bog waters, sedimentary basinal brines, sediment porewaters and sediment-hosted geothermal systems (Bruckert, 1970; Graustein et al., 1977; Thurman, 1985; MacGowan and Surdam, 1988; Sposito, 1989; Martens, 1990). Organic acids and their anions may play a number of roles in governing the behavior of PGE in the environment including (Wood, 1996): 1) increased solubility or decreased sorption owing to the formation of dissolved complexes or a decrease in pH; 2) formation of colloidal particles; 3) reduction; 4) modification of the surface properties of minerals; 5) modification of the rates of various reactions; and 6) modification of bioavailability and/or toxicity. In this paper we restrict consideration to the formation of aqueous complexes of  $\text{Pd}^{2+}$  with organic ligands.

## Experimental studies

Relatively few experimental studies of the complexation of  $\text{Pd}^{2+}$  with naturally occurring organic ligands have been conducted. Using ion exchange, Nabivanets and Kalabina (1972) have measured a stability constant for the Pd-oxalate complex  $\text{Pd}(\text{ox})^0$  at 18°C and 0.2 M ionic strength of  $\log K_1 \approx 8.7$ . Their results indicate that the Pd-oxalate complex is quite strong. Li and Byrne (1990) used absorption spectroscopy to show that amino acids can form strong complexes with  $\text{Pd}^{2+}$  and these complexes may dominate Pd speciation in seawater. Bowles et al. (1995) have conducted experiments which suggest that Pt and Pd are taken up by solid HS, and that dissolved HS can result in the solubilization of these metals in aqueous solutions.

Solubility and spectroscopic studies of the interaction of Pd(II) and fulvic acid, acetate, oxalate, phthalate and salicylate have been conducted by Wood et al. (1994). The latter two organic ligands were investigated as analogues of the predominant binding sites on HS. Wood et al. (1994) reported that the presence of 44.8 mM acetate, 21.3 mM phthalate, 27.9 mM salicylate or 149 mg/L Armadale Bh fulvic acid inhibited the precipitation of  $\text{Pd}(\text{OH})_2(\text{amorphous})$  from supersaturated solutions at 25°C over various pH ranges (all solutions also contained 22.4 mM chloride ion). For example, in the absence of organic ligands, 1 mM Pd in

solution begins to precipitate at a pH near 4. In the presence of 44.8 mM acetate, precipitation of the same solution is postponed until a pH near 6. Phthalate shows similar behavior. On the other hand, salicylate did not prevent precipitation at pH 4, but did prevent precipitation between pH 6 and 12. The fulvic acid apparently prevented precipitation over the entire pH range from 4 to 12, but there was a lack of data between pH 7 and 11. These experiments clearly indicate an important effect of the organic acids on the solubility of  $\text{Pd}(\text{OH})_2$ , but do not necessarily prove complexation. Therefore, spectroscopic investigations were carried out. UV-visible absorption, Raman and IR spectroscopy verified that acetate, oxalate, phthalate and salicylate indeed form complexes with  $\text{Pd}^{2+}$ .

The UV-visible absorption spectroscopic results of Wood et al. (1994) for Pd-oxalate recently have been confirmed and extended by investigating a wider range of Pd, NaCl and oxalate concentrations. A set of representative example spectra are given in Fig. 1.

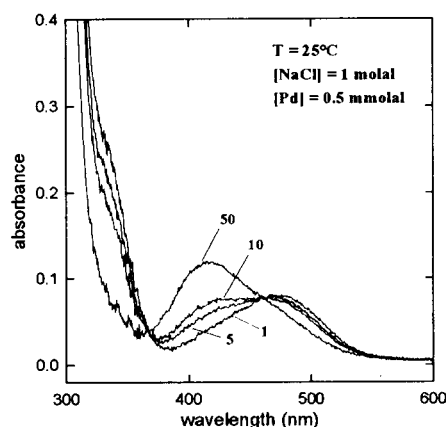


Figure 1: Absorption spectra of solutions containing 1 molal NaCl, 0.5 mmolal Pd and the indicated concentrations of oxalate ion.

The spectra in Fig. 1 demonstrate a distinct change in the predominant Pd(II) species with increasing oxalate concentration from 1 to 50 mmolal. The existence of isosbestic points in Fig. 1 indicate the presence of only two main species. These spectra and those presented in Wood et al. (1994) and Wood (1996), show conclusively that oxalate forms aqueous complexes with  $\text{Pd}^{2+}$ . Additional work is in progress that should permit derivation of stoichiometries and stability constants of the Pd-oxalate species using absorption spectroscopy.

In order to determine the stoichiometry and stability constants of possible Pd-acetate complexes, Pickrell (1997) measured the solubility of  $\text{Pd}(\text{OH})_2$  as a function of acetate concentration at 25°C, pH = 4.4 and  $I = 1.0 \text{ m NaClO}_4$ . The results are given in Fig. 2. The solubility exhibits a clear increase with increasing free acetate concentration, and the data conform to a straight line with a slope of approximately 2. The data imply the formation of a complex with the stoichiometry  $\text{Pd}(\text{ac})_2^0$  and a cumulative stability constant of  $\log \beta_2 = 9.2$ . Comparing this value to the cumulative stability constant for  $\text{PdCl}_2^0$  determined by Elding (1972) at the same ionic strength ( $\log \beta_2 = 7.76$ ) it is apparent that the acetate complex is more than an order of magnitude more stable than its chloride counterpart. Again, the stability of the Pd(II)-acetate and -oxalate complexes is somewhat surprising in light of Pearson's

(1963) hard-soft acid-base theory, but may be related to the surprising stability of Pd(II)-hydroxide complexes and, in the case of oxalate, the ability to form bidentate complexes.

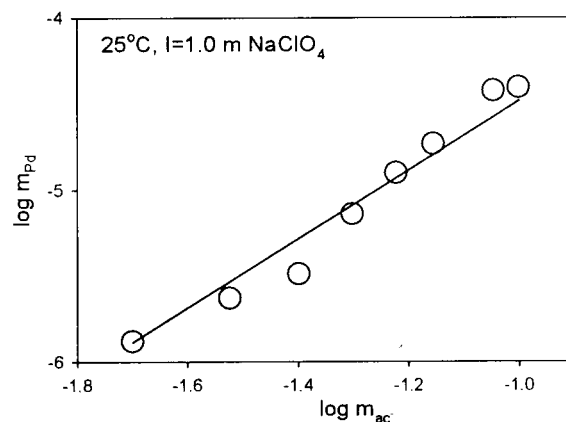


Figure 2: Solubility of  $\text{Pd}(\text{OH})_2$ (amorphous) as a function of free acetate concentration.

### Implications

In order to determine the importance of Pd-oxalate and -acetate complexes relative to Pd-chloride and -hydroxide complexes in a "typical" soil solution at 25°C, the distribution of Pd among the following species was calculated (Fig. 3):  $\text{Pd}^{2+}$ ,  $\text{Pd}(\text{ac})_2^0$ ,  $\text{Pd}(\text{ox})^0$ ,  $\text{PdCl}^+$ ,  $\text{PdCl}_2^0$ ,  $\text{PdCl}_3^-$ ,  $\text{PdCl}_4^{2-}$ ,  $\text{PdCl}_3\text{OH}^{2-}$ ,  $\text{Pd}(\text{OH})_2^0$  and  $\text{Pd}(\text{OH})_3^-$ . The stability constant for  $\text{Pd}(\text{ox})^0$  from Nabivanets and Kalabina (1972) and that for  $\text{Pd}(\text{ac})_2^0$  quoted above were employed. The required stability constants for the Pd-chloride complexes come from Elding (1972) and those for the Pd-hydroxychloride and -hydroxide complexes come from Pickrell (1997). The concentrations of total chloride, acetate and oxalate employed in the calculations are given in the caption to Fig. 3 and represent typical concentrations of these anions in soil solutions.

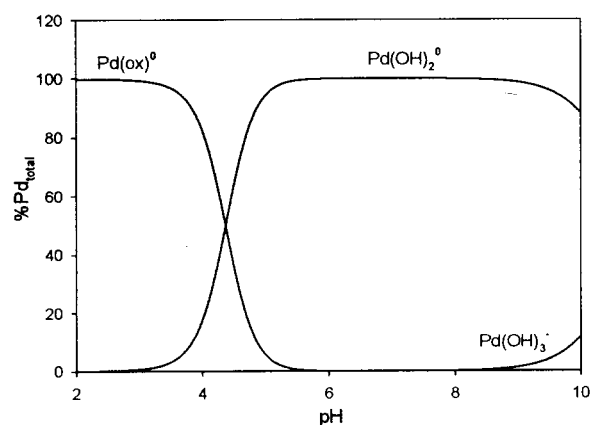


Figure 3: Diagram showing the distribution of Pd(II) species at 25°C in a model soil solution containing  $6 \times 10^{-6} \text{ M}$  total chloride,  $10^{-4} \text{ M}$  total oxalate and  $10^{-4} \text{ M}$  total acetate. Species amounting to less than 1% at all pH values are omitted for clarity.

Fig. 3 shows that, relative to oxalate and hydroxide complexes, Pd-acetate complexes are weak, and probably do not play an important role in soils. Palladium-oxalate complexes may be the predominant dissolved Pd species in acidic, organic-rich soils, but above a pH of approximately 4, hydroxide complexes predominate.

The stability constants of Pd-fulvate complexes remain unknown. However, given their generally higher concentrations in most natural waters and their greater complexation capacity compared to simple carboxylate anions, such complexes may play an important role in the biogeochemical cycling of Pd and, by extension, other PGE, in the environment. Binding sites of fulvic acid containing S- and N-atoms may be particularly important.

### Other PGE

There is almost no information on the ability of geologically relevant, simple carboxylate ligands or humic substances to complex the other PGE, i.e., platinum, ruthenium, rhodium, iridium, and osmium. A study by Wood (1990) showed that fulvic acid and phthalate were effective in maintaining Pt in a hydromorphically transportable form, although it was not clear whether this was a result of the formation of aqueous complexes or colloids, or was a kinetic effect. Salicylate had a much weaker effect. Thiosalicylate exhibited a very strong affinity for Pt, consistent with the known affinity of reduced S-bearing ligands for Pt, but this organic ligand is relatively insoluble in water. The author is unaware of any studies on the complexation of Rh, Ru, Ir or Os with the organic ligands considered in this paper. The lack of knowledge of the nature and thermodynamics of the interaction of PGE with environmentally important organic ligands makes additional research desirable.

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