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Selective sorption of noble metals by an organomercury sorbent

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Organomercury sorbents have been found to absorb noble metals from aqueous solutions.

The sorption concentration of transition metals, including gold and platinum group metals, from aqueous solutions has been thoroughly investigated since it was first discovered.[1] Highly effective sorbents for noble metals have been found, but sorption on them is by ion-exchange[2] or complexing[3] mechanisms. Though it is well known[4] that noble metals can form sufficiently stable organometallic compounds (OMC), nevertheless, sorption processes based on formation of OMC has not been studied before. Organomercury salts (OMS) RHgX (R = hydrocarbon radical, X = halogen or acetate) are the most promising OMC due to their stability in aqueous solution, even in an acid medium (pH = 1–3), and the simplicity of chemical immobilization[5] on a silica gel surface.

We found that silica gels **1**–**3** modified by arylmercurioacetic functional groups (Scheme 1) could be utilized as highly selective sorbents for the sorption of some noble metals M from aqueous solutions of their anionic halogen complexes such as MX_n.

In the model reaction of phenylmercury chloride PhHgCl with complexes of palladium, platinum(II), platinum(IV) and gold(III), low reaction activities were obtained (Table 1). Platinum complexes did not react with PhHgCl, but $PdCl_4^{2-}$ was completely reduced in 12 h:

$$2PhHgCl + PdCl_4^{2-} \longrightarrow Ph{-}Ph + 2HgCl_2 + Pd + 2Cl^- \qquad (1)$$

Under the same conditions only 25% of gold (as $AuCl_4^-$) was reduced in 70 h.

Reactions with fixed OMS usually run at a sufficiently high rate (*e.g.* reaction of $PdCl_4^{2-}$ with OMS type **1** immobilized on silica gel with surface area 250 $m^2\,g^{-1}$ and content of active groups – ‘capacity’ – 0.36 mmol OMS groups per gram was completed in 1 h). This was confirmed by spectrophotometry. Notably, in this case, metallic palladium forms a colloidal precipitate in the pores of the sorbent, colouring silica gel black.

$$2\,\boxed{SiO_2}{-}C_6H_4{-}HgOAc + PdCl_4^{2-} \longrightarrow \boxed{SiO_2}{-}C_6H_4{-}C_6H_4{-}\boxed{SiO_2} + Pd + HgCl_2 \qquad (2)$$

The sorption process rate depends upon three factors: initial concentration of palladium, sorbent surface area and active group surface concentration. The reaction obeys first-order kinetics for these factors.

According to chemical[6] and X-ray fluorescence[7] analysis data, less than half of the OMS groups (0.18 mmol g^{-1}) reacted with $PdCl_4^{2-}$ and 0.09 mmol g^{-1} of palladium was sorbed. In separate work using the ESCA method (X-ray photoelectron spectroscopy) metallic palladium was not detected on the sorbent surface. Probably this is a result of the low surface density of the OMS groups on silica gel (groups per nm^2). One can believe that the reaction takes place only when the distance between two OMS groups is not more than 2 nm (overall length of the C–C bonds in two fixed radicals). Unreacted OMS groups can be destroyed by heating the sorbent with an aqueous solution of iodine and KI (iododemercuration) while the residual mercury can be completely removed from the sorbent.

$$\boxed{SiO_2}{-}C_6H_4{-}HgOAc + I_2 + 3I^- \longrightarrow \boxed{SiO_2}{-}C_6H_4I + HgI_4^{2-} \qquad (3)$$

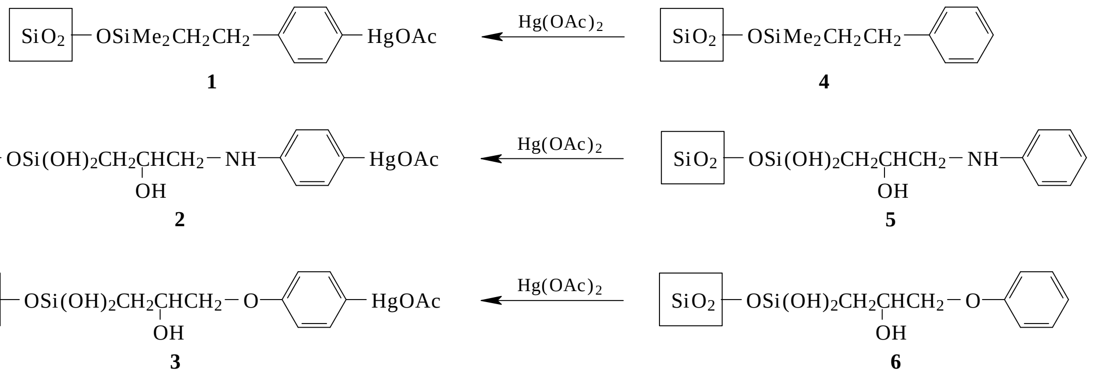
Colloidal metallic palladium can also be removed by treatment of the sorbent with concentrated nitric acid, or a mixture of it with hydrochloric acid (aqua regia).

Fixed OMS types **2** and **3** have similar characteristics with Pd^{II}, but their capacity is significantly lower in comparison with type **1** due to the low surface density of OMS groups on silica gel (groups nm^{-2}) and lower surface area (Table 2).

The cationic complex of palladium $Pd(NH_3)_4^{2+}$ did not react with immobilized OMS. This possibly confirms that sorption process (2) includes an anionic exchange step (4).

We also investigated the reaction between compounds of non-ferrous metals (such as Cu, Ni, Co) and fixed OMS (Table 3). The sorption of base metals does not take place on an OMC sorbent, but some noble metals (as halide anions) are sorbed with accompanying reduction to the metallic state. Remarkably, platinum(II) and (IV) have different reaction mechanisms. While platinum(II) is reduced in a similar manner to palladium(II), platinum(IV) is sorbed without reduction, probably through an ion-exchange mechanism (4).

Sorbent capacities are quite different for the noble metals, but in any case they are always significantly lower than the overall number of OMS groups. When palladium and platinum(II) are sorbed, the ratio of OMS groups to metal atoms



Scheme 1

$$\boxed{\mathrm{SiO_2}}-\mathrm{C_6H_4-Hg-OAc} + \mathrm{PtCl_6^{2-}} \longrightarrow$$

$$\boxed{\mathrm{SiO_2}}-\mathrm{C_6H_4-Hg-PtCl_6^{-}} + \mathrm{OAc^{-}} \qquad (4)$$

is 4–5 to 1. The ratio mentioned above is 12 to 1 when gold(III) is sorbed. This phenomenon can be described by the reducing mechanism of sorption. According to this mechanism, to reduce gold(III) to the metal state, three OMS groups are required instead of two arranged rather closer to each other. It is obvious that the probability of such an arrangement occurring for two groups is considerably higher than for three.

Table 1 Reaction of noble metals/halide anions ($C_0 = 1.00\times10^{-3}$ mol) with phenylmercury chloride in aqueous solution at pH = 2 (followed by UV spectroscopy).

Anion	Time/h	Final anion concentration/mol dm^{-3}	Found Ph$_2$/mol dm^{-3}
$PdCl_4^{2-}$	12	0	5×10^{-4}
$PtCl_4^{2-}$	72	1.0×10^{-3}	0
$PtCl_6^{2-}$	72	1.0×10^{-3}	0
$AuCl_4^{-}$	72	7.5×10^{-4}	2.4×10^{-4}

Table 2 Sorption capacity of OMS sorbents ($C = 1.0\times10^{-3}$ mol, pH = 2, 20 °C, 1 h, see Scheme 1).

Type of fixed OMS	Metal complex	Overall amount of fixed OMS groups/mmol g^{-1}	Sorption/ mmol g^{-1}
1	$PdCl_4^{2-}$	0.36	0.09
1	$PdCl_4^{2-}$	0.22	0.05
2	$PdCl_4^{2-}$	0.14	0.05
3	$PdCl_4^{2-}$	0.05	0.01
1	$AuCl_4^{-}$	0.36	0.031
1	$AuCl_4^{-}$	0.22	0.015
1	$PtCl_4^{2-}$	0.22	0.046[a]
1	$PtCl_6^{2-}$	0.22	0.054

[a] 24 h.

Table 3 Concentration of transition metal compounds from aqueous solutions (5 ml solution with 0.100 g fixed OMS type **1** on silica gel).

No.	Compound	Concentration/ mol dm^{-3}	pH[a]	Time/h	Recovery of metal (%)[b]
1	$CuSO_4$	0.0160	3.0	6	< 0.025
2	$NiSO_4$	0.028	3.0	6	< 0.014
3	$CoSO_4$	0.030	3.0	6	< 0.013
4	K_2PdCl_4	0.001	1.5	1	100
5[c]	K_2PdCl_4	1.0×10^{-6}	1.5	24	90
6	H_2PtCl_6	0.0010	1.5	24	42
7	K_2PtCl_4	0.0010	1.5	24	92
8	$HAuCl_4$	0.0010	1.5	1	92
9	H_2IrCl_6	0.0010	1.5	6	< 0.01
10	$CuSO_4$ K_2PdCl_4	0.016 0.0010	1.5	6	< 0.03 92

[a] pH was kept up with HCl. [b] By X-ray fluorescent analysis, S_r = 3%. [c] 1 dm^3 of the solution was used.

Owing to this reducing mechanism of sorption, organomercuric sorbents are highly selective for platinum group metals. We found (Table 3) that if the concentration of base metal ions (Cu^{2+}, Ni^{2+} or Co^{2+}) exceeds the concentration of Pd^{II} by 5–50 times, recovery of palladium decreases by 10–20%. Sorption of non-ferrous metals remains variable and the calculated concentration index is > 10^4.

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