

## SORPTION AND SEPARATION OF PALLADIUM, PLATINUM AND GOLD CHLOROCOMPLEXES BY MEANS OF A DIPICOLINIC ACID POLYSTYRENE-BASED CHELATING RESIN

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(Received June 13, 1990; accepted in revised form October 13, 1990)

*A chelating ion-exchange resin containing dipicolinic acid as functional group and based on microporous chloromethylated cross-linked polystyrene–divinylbenzene (2%) copolymer has been prepared. Its sorption and desorption characteristics for Pd(II), Pt(II), Pt(IV) and Au(III) have been studied in aqueous chloride solutions under a number of experimental conditions, both in batch and in column, at room temperature and constant ionic strength ( $\mu = 1$  mol/l, KCl/HCl). In column operations at pH 6, Pd(II) can be separated from Pt(II) or Pt(IV) owing to the different rate of formation of the immobilized chelated species. From a mixture of Pd(II), Pt(IV) and Au(III) at pH 6, Pt(IV) flows unaffected, whereas Au(III) and Pd(II) are both retained and successively separated by selective elution. From the same mixture at pH  $\leq 0$  only Au(III) is sorbed by anionic exchange.*

### INTRODUCTION

Selective complexation for separation and recovery of metal ions, especially from dilute aqueous solutions, is the main object of chelating resins. For this purpose a large number of different chelating ligands have been incorporated into polymer matrices, with preference for the polystyrene-based polymers [1,2], as these are chemically stable under the conditions of use. The hydrophobic character of the polystyrene backbone which

affects unfavourably the access of metal ions to the chelating groups in the resin has been partially overcome by introducing into the polymer network hydrophilic ligands. One of the most extensively studied ion-exchange chelating resins is that containing imino-diacetic acid (IDA) groups. This resin, commercially available under different trade names, has been found suitable for separation and preconcentration of metal ions [3] and, in particular, it is effective in sequestering Fe(III) [4]. Following the success of this resin a wide

variety of ion-exchangers containing ligands similar to iminodiacetic acid have been prepared and studied [2].

Recently it has been found that 2,6-pyridinedicarboxylic acid (L), an analogue of IDA, reacts in aqueous solution at very different rates with  $\text{PtCl}_4^{2-}$  and  $\text{PdCl}_4^{2-}$  anions to give mono-anionic  $[\text{Me}(\text{L}-2\text{H})\text{Cl}]^-$  (Me = Pt, Pd) and neutral  $[\text{Me}(\text{L}-\text{H})_2]$  (Me = Pt, Pd) square planar tetracoordinate compounds, which have been separated in the solid state and characterized [5-7]. In addition, fast coordinative interaction has been observed spectrophotometrically by reaction of  $\text{AuCl}_4^-$  with L, even if no solid product has been isolated. On the other hand, no reaction has been observed with  $\text{PtCl}_6^{2-}$ . Based on these features, it was then expected that a resin containing dipicolinic acid groups would be suitable to separate the above mentioned metal ions. In the present paper the preparation and the sorption behaviour of a dipicolinic acid polystyrene-based chelating resin towards Pd(II), Pt(II), Pt(IV) and Au(III) chloro-anions, both in batch conditions and in column, as well as the recovery of the sorbed metal ions, are reported.

## EXPERIMENTAL

### Materials and methods

Unless specified, all solvents and reagents (Aldrich and Fluka) were used without further purification. Crystalline  $\text{K}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_2[\text{PtCl}_4]$ ,  $\text{K}_2[\text{PtCl}_6]$  and  $\text{K}_2[\text{PdCl}_4]$  were prepared from high purity metals by standard methods. Microporous chloromethylpolystyrene cross-linked with 2% DVB (200-400 mesh, 2.3 meq Cl/g, surface area  $44.25 \pm 0.01 \text{ m}^2/\text{g}$ ) was purchased from Fluka.

I.R. spectra were recorded on a Perkin-Elmer 683 or on a Bio-Rad Digilab FTS-40 spectrophotometer. U.V. spectra were taken

on a Perkin-Elmer Lambda 5 spectrophotometer using matched 1 cm quartz cells. Metal ion concentrations were measured with a Perkin-Elmer 2380 atomic absorption spectrophotometer. Elemental analysis were performed by the Microanalytical Laboratory of the University of Padua. Surface area (B.E.T.) was determined with a Carlo Erba Sorptomatic 1800 instrument.

### Synthesis of the resin

#### 2,6-Dimethoxycarbonyl-4-hydroxypyridine (1) and [(2,6-dicarboxymethyl-4-pyridyl)oxymethyl]polystyrene (2)

Compounds (1) and (2) were prepared according to the published procedure [8]. Analysis for 2: calc. (%) for  $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.71}(\text{C}_{18}\text{H}_{17}\text{NO}_5)_{0.27}$ : C, 78.2; H, 6.4; N, 2.3. Found: C, 78.0; H, 6.2; N, 2.3.

#### Potassium[(2,6-dicarboxylate-4-pyridyl)oxymethyl]polystyrene (3)

A suspension of (2) (18.5 g, 30.34 meq of nitrogen) in 450 ml of 1,2-dichloroethane was treated with 150 ml of an aqueous solution of 50% KOH containing Adogen 464 (5 g), and the resulting mixture was allowed to react for 48 h at 70°C under stirring and an atmosphere of nitrogen. After cooling the solid was filtered off, washed exhaustively with  $\text{H}_2\text{O}$ , MeOH,  $\text{H}_2\text{O}$ , THF/ $\text{H}_2\text{O}$  (3:1, v/v), THF, acetone, dichloromethane and finally with  $\text{H}_2\text{O}$  to neutral pH. The resin was then dried under vacuum for 24 h at 50°C. I.R. (KBr pellets):  $1620 \text{ cm}^{-1}$  [s, b;  $\nu$  ( $\text{COO}^-$ )]. Analysis: calc. (%) for  $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.71}(\text{C}_{16}\text{H}_{11}\text{NO}_5\text{K}_2)_{0.27}$ : C, 69.0; H, 5.0; N, 2.1. Found: C, 68.5; H, 5.5; N, 2.1.

### Stability

In order to estimate the stability of the resin in acid solutions, four portions of the resin (100 mg) were shaken with 10 ml of HCl 0.1 M, 1 M, 2 M and 12 M, respectively,

for 7 days. The content of released chelidamic acid was determined spectrophotometrically by comparison with the spectra of solutions of chelidamic acid under the same acidity conditions.

### Analysis

Atomic absorption spectrophotometry was used for analysis of metal ions in solution. The extent of sorption of metal ions was calculated from the difference of metal concentrations in the substrate before and after sorption by the resin and/or in the solutions after stripping or elution with 2 *M* HCl or 1 *M* KCN.

### Sorption experiments

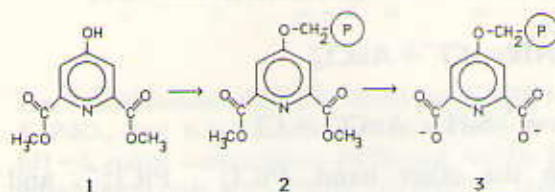
A batch technique was used to study metal ions uptake as a function of pH, sorption rate behaviour and sorption isotherms. Measured amounts of the resin, equilibrated in 25 ml aqueous solutions at the desired pH values, were vigorously shaken with 25 ml aqueous solutions of known concentrations of  $K[AuCl_4] \cdot 2H_2O$ ,  $K_2[PtCl_4]$ ,  $K_2[PtCl_6]$ , and  $K_2[PdCl_4]$ , at the same pH values in tightly stoppered flasks for 48 h at 25°C, using an oscillatory shaker with 3 cm stroke at 80 cyclings  $min^{-1}$ . The equilibrium sorption was calculated from the residual metal concentration of the sorbate in the equilibrated solution or after stripping of the metal ion. All the experiments were made at constant ionic strength ( $\mu = 1$  mol/l, KCl/HCl), which also prevents the formation of solvolyzed species of Pd(II) and Au(III). Separations of mixtures of metal ions were performed in small glass columns (25 cm length, 0.6 cm inside diameter). Resin (1 g) was packed into the column and equilibrated with aqueous solutions ( $\mu = 1$  mol/l, KCl/HCl) at fixed working pH values. Metal solutions (10 or 20 ml) were percolated through the column at a rate of 8 ml  $h^{-1}$ . Both effluents and eluates with

HCl 2 *M* or KCN 1 *M* were collected and diluted to 25 ml in volumetric flasks and analyzed by atomic absorption spectrophotometry.

## RESULTS AND DISCUSSION

### Synthesis and characterization of the resin

The synthesis of the resin is summarized in Scheme 1. The reaction of 2,6-dimethoxycarbonyl-4-hydroxypyridine (1) with chloromethylpolystyrene, in the presence of  $Cs_2CO_3$  provided resin (2) from which resin (3) was obtained by base hydrolysis under phase-transfer catalyzed conditions with 100% conversion, corresponding to a loading of 1.49 mmol ligand per gram of dry resin in the potassium form. The infrared spectrum of (3) shows two bands at 1620 and 1405  $cm^{-1}$  for the asymmetric and symmetric stretching vibrations of the carboxylate anions, respectively. Whereas it does not exhibit any band at 1725  $cm^{-1}$  for the ester precursor (2). The resin in the potassium form can be converted to the acid form by equilibration with HCl 2 *M*; in this form the infrared spectrum shows a broad band centered at 1740  $cm^{-1}$  due to the stretching vibration of the carboxylic groups while the carboxylate bands at 1620 and 1405  $cm^{-1}$  have disappeared. The resin proved to be stable in 2 *M* HCl, whereas a release of chelidamic acid corresponding to 2% of that theoretically bound to the resin was detected after seven days of contact with concentrated HCl.



Scheme 1

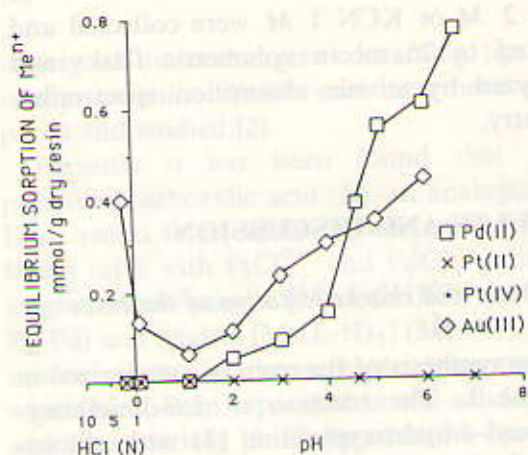
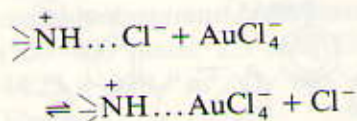


Fig. 1. Effect of pH on equilibrium sorption of  $\text{Me}^{n+}$ . Initial concentration of solutions, 4 mmol/l  $\text{Me}^{n+}$  as chloro anions; resin charge 2.89 g(wet)/l; temperature 25°C.

### Batch experiments

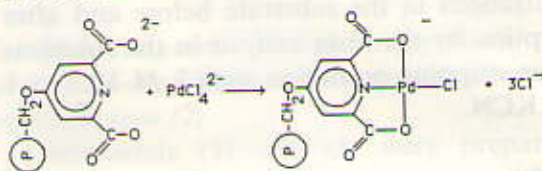
#### Effect of pH on sorption

The sorption behaviour of the resin toward  $\text{AuCl}_4^-$ ,  $\text{PtCl}_4^{2-}$ ,  $\text{PtCl}_6^{2-}$  and  $\text{PdCl}_4^{2-}$  was investigated in aqueous solutions in the pH range 0–7 ( $\mu = 1$  mol/l, KCl/HCl) and in 2 N HCl. The pH profiles of the equilibrium sorption are shown in Fig. 1. Pt(II) and Pt(IV) are not sorbed at any examined pH, whereas sorption capacities for Au(III) and Pd(II) are maximal at pH 6 and pH 6.5, respectively, and decrease continuously to pH 1.1. Sorption experiments at higher pH are not possible due either to reduction to metallic gold or precipitation of hydroxo species of palladium(II) for pH values above 6 and 6.5, respectively. The  $\text{AuCl}_4^-$  sorption capacity of the resin, however, increases again at pH < 1.1 in HCl media and this may be attributed to the anion exchange reaction



On the other hand,  $\text{PtCl}_4^{2-}$ ,  $\text{PtCl}_6^{2-}$ , and  $\text{PdCl}_4^{2-}$  are not sorbed at all under the same

experimental conditions and this may be ascribed to competition of the chloride ion with the resin ligand. These results agree with previous findings on chloro complexes of gold and platinum metals which clearly indicate that the strength of electrostatic interaction is highly dependent on the charge of the complex and the preference in anion exchange for large singly charged anions [9].  $\text{PdCl}_4^{2-}$  is likely to be sorbed by the resin at pH 6–6.5 through chelation, according to the following reaction:



as deduced by comparing the I.R. spectrum of the resin saturated with  $\text{PdCl}_4^{2-}$  at pH 6 with that of a sample of  $\text{K}[\text{Pd}(\text{L-2H})\text{Cl}]$  prepared independently [7]. The former showed two bands centered at 1665 and 308  $\text{cm}^{-1}$ , whereas the latter two bands at 1670 and 308  $\text{cm}^{-1}$ , which can be assigned to the coordinated  $-\text{COO}$  and  $\text{Pd}-\text{Cl}$  stretching vibrations, respectively.

The I.R. spectrum of the resin saturated with  $\text{AuCl}_4^-$  at pH 6 exhibited three significant relatively broad bands centered at 1715, 1615 and 355  $\text{cm}^{-1}$ , not present in the spectrum of the chelating resin. The bands at 1715 and 355  $\text{cm}^{-1}$  can reasonably be assigned to coordinated  $-\text{COO}$  and  $\text{Au}-\text{Cl}$  stretching vibrations, respectively, on the basis of assignments made on the correlated complex  $[\text{Au}(\text{pic})\text{Cl}_2]$  [10] (pic = 2-pyridinecarboxylate), in which case coordinated  $-\text{COO}$  and  $\text{Au}-\text{Cl}$  stretching vibrations occurred at 1705 and 380  $\text{cm}^{-1}$ . The third band in the spectrum of the resin at 1615  $\text{cm}^{-1}$  is likely to be due to the asymmetric stretching of free carboxylate anion  $-\text{COO}^-$ . These features suggest that at pH 6 the dipicolinate behaves as a bidentate ligand towards Au(III), giving

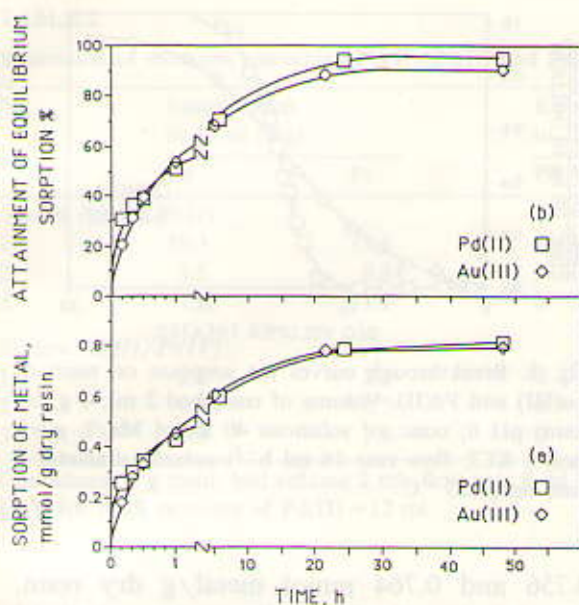


Fig. 2. (a) Rate of sorption by resin of Pd(II) and Au(III) from  $K_2PdCl_4$  and  $KAuCl_4$  solutions ( $\mu = 1$  mol/l, KCl, pH 6, initial concentration 40 mmol/l). (b) Rate of attainment of equilibrium sorption. Resin charge 2.89 g(wet)/l; temperature 25°C.

rise to immobilized tetracoordinated dichloro species. The I.R. spectrum of the resin loaded with Au(III) in 2 M HCl showed in the same region only the band at  $1740\text{ cm}^{-1}$  characteristic of free carboxylic groups not involved in chelation.

#### Kinetic behaviour

The kinetic behaviour of the resin towards  $PdCl_4^{2-}$  and  $AuCl_4^-$  was studied at pH 6 under vigorous agitation at room temperature. In order to obtain the rate of fractional attainment of equilibrium sorption as a function of time, the data were divided by the corresponding sorption values measured at equilibrium. The results plotted in Fig. 2 show that the resin has relatively slow sorption kinetics either for  $PdCl_4^{2-}$  or  $AuCl_4^-$ , the 50% of the equilibrium sorption ( $t_{1/2}$ ) being reached in about 60 minutes. This is consistent with the low surface area ( $44.25 \pm 0.01\text{ m}^2/\text{g}$ ) and the styrenic character of the resin, due to

the rather low functionalization level given that the original chloromethyl capacity is only  $2.3\text{ mmol g}^{-1}$ . The ability of the resin to function in ion exchange is therefore due to the presence of ionized groups [11,12] which allow the swelling in aqueous solutions. In the potassium form the resin has a water regain [13] of  $0.51\text{ g g}^{-1}$ , consistent with the measured  $t_{1/2}$  and comparable with values reported in the literature for other polystyrene resins [13].

#### Sorption isotherm for Pd(II) and Au(III)

The sorption capacity of the resin for Pd(II) and Au(III) chloride anions as a function of metal ion concentration was examined at pH 6. The equilibrium sorption data are plotted in Fig. 3. Data treatment revealed that sorption conformed to Langmuir isotherm equation:

$$\chi = 10^{-3}K_b A_s C_A / (1 + 10^{-3}K_b C_A) \quad (1)$$

where  $\chi$  is the equilibrium sorption (mmol Me/g dry resin),  $C_A$  is the equilibrium sorbate concentration (mmol Me/l),  $A_s$  is the saturation capacity (mmol Me/g dry resin), and  $K_b$  is the binding constant (l/mol). The values of Langmuir isotherm parameters ( $A_s$  and  $K_b$ ) were determined by least-squares fit (Fig. 4)

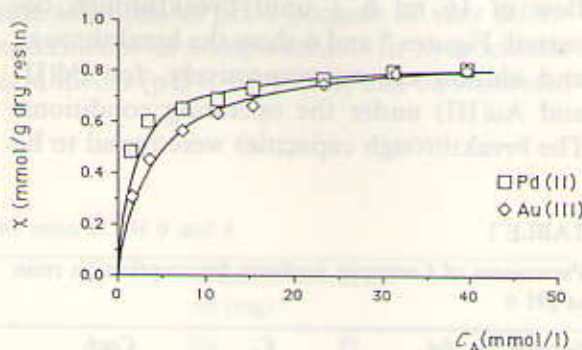


Fig. 3. Equilibrium sorption of Pd(II) and Au(III) from  $K_2PdCl_4$  and  $KAuCl_4$  solutions ( $\mu = 1$  mol/l, KCl, pH = 6, initial concentration Pd(II) and Au(III) 2–40 mmol/l) and resin. Resin charge 2.89 g(wet)/l. Temperature 25°C.

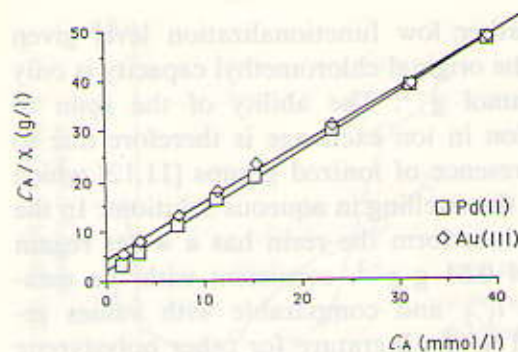


Fig. 4. Linearization of equilibrium sorption curves of Fig. 3.

plotting  $C_A/\chi$  versus  $C_A$ . The results are given in Table 1. The values of the binding constant  $K_b$  in eqn. (1) for Pd(II) (548 l/mol) and Au(III) (245 l/mol) account for the weaker dependence of sorption capacity of Pd(II) than Au(III) on the solution concentration.

#### Column separation experiments

The possibility to use the resin for selective column separation of the metal ions examined was investigated by column tests. In order to determine the column capacities at pH 6 and stripping conditions for Pd(II) and Au(III), breakthrough and elution studies were carried out on a 1 g resin column (2 ml bed volume). A 40 mmol/l solution of metal ion was passed through the column resin at a flow of 16 ml h<sup>-1</sup> until breakthrough occurred. Figures 5 and 6 show the breakthrough and elution curves, respectively, for Pd(II) and Au(III) under the operating conditions. The breakthrough capacities were found to be

TABLE 1

Parameters of Langmuir isotherm for sorption on resin at pH 6

Sorbate	$A_s$ (mmol/g dry resin)	$K_b$ (l/mol)	Corr. coeff.
PdCl <sub>4</sub> <sup>2-</sup>	0.840	548	0.999
AuCl <sub>4</sub> <sup>-</sup>	0.888	245	0.998

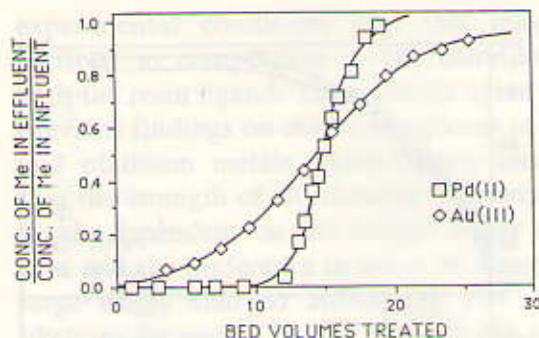


Fig. 5. Breakthrough curves for sorption on resin of Au(III) and Pd(II). Volume of resin bed 2 ml; 1 g dry resin; pH 6; conc. of solutions 40 mmol Me/l;  $\mu=1$  mol/l, KCl; flow rate 16 ml h<sup>-1</sup>; column diameter 6 mm; temp. 25 °C.

0.756 and 0.764 mmol metal/g dry resin, respectively. Similar values were obtained from equilibrium sorption measurements. This suggests a high utilization of the column capacity.

The results summarized in Table 2 indicate that when Pd(II)-Pt(II) or Pd(II)-Pt(IV) mixtures of varying molar ratios were passed through a column of the resin at pH 6, Pd(II) can be successfully separated from Pt(II) or Pt(IV). In every separation Pd(II) was completely sorbed while Pt(II) or Pt(IV) were not retained at all. A 100% recovery of the Pd(II) retained on the column could be achieved by

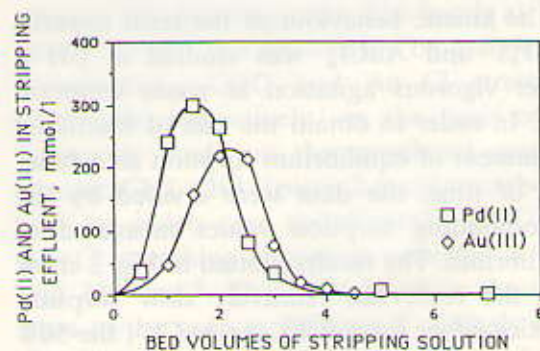


Fig. 6. Stripping of resin columns (bed volume 2 ml) loaded with Pd(II) and Au(III) (0.756 and 0.764 mmol/g, respectively). Flow rate of stripping solutions (2 N HCl for Pd and 1 M KCN for Au): 16 ml h<sup>-1</sup>.

TABLE 2

Separation of mixtures containing Pd(II)/Pt(II) and Pd(II)/Pt(IV) by the resin at pH 6

No.	Initial concn. in 10 ml (mg)		Effluent concn. in 25 ml (mg)		Eluate concn. in 25 ml 2 M HCl (mg)	
	Pd	Pt	Pd	Pt	Pd	Pt
<i>System Pd(II)/Pt(II)</i>						
1	10.3	11.8	0	11.8	10.3	0
2	1.1	0.84	0	0.84	1.05	0
3	1.1	31.2	0	31.2	1.05	0
<i>System Pd(II)/Pt(IV)</i>						
1	2.1	1.5	0	1.5	2.1	0
2	0.23	1.7	0	1.7	0.23	0
3	22.3	1.8	0	1.8	22.3	0

Conditions: 1 g resin, bed volume 2 ml; flow rate 8 ml h<sup>-1</sup>;  $\mu = 1$  mol/l KCl (initial solutions); eluent volume (2 M HCl) for 100% recovery of Pd(II) = 12 ml.

eluting with 12 ml (6 bed volumes) of 2 M HCl.

As shown in Table 3, separation of Au(III) from Pd(II) and Pt(IV) is also possible. To accomplish this separation a solution at pH 0 containing a mixture of the three metal chloride anions was passed through 1 g resin column equilibrated at the same pH. Only AuCl<sub>4</sub><sup>-</sup> was retained on the resin by ion exchange. It was partially eluted with water (5 ml) and finally with 1M KCN (12 ml, 6 bed volumes). The effluent solution containing Pd(II) and Pt(IV), after neutralization to pH 6, was percolated into a second column their separation being accomplished according to the conditions in the paragraph above.

An alternative separation procedure, start-

ing from a mixture of the three metal chloride anions at pH 6, was also developed. In this case, Au(III) and Pd(II) were quantitatively retained on the column while Pt(IV) was not. Then Pd(II) was selectively eluted with 2 M HCl while Au(III) was completely retained on the resin by anion exchange. Finally, Au(III) was eluted with water and 1 M KCN.

## CONCLUSIONS

The resin allows a selective separation of Pd(II) from Pt(II) or Pt(IV) in aqueous chloride solutions at pH 6 because of very different kinetics of complexation. In hydrochloric acid media (pH  $\leq$  0) Au(III) can be separated

TABLE 3

Separation of mixtures containing Pd(II)/Pt(IV)/Au(III) by the resin at pH 0 and 6

pH	Initial concn. in 20 ml (mg)			Effluent concn. in 25 ml (mg)			Eluate concn. in 25 ml (mg) <sup>a,b</sup>		
	Pd	Pt	Au	Pd	Pt	Au	Pd	Pt	Au
0	11.46	8.11	11.0	11.46	8.11	0	0	0	11.0 <sup>b</sup>
6 <sup>c</sup>	10.98	9.6	10.5	0	9.6	0	10.98 <sup>a</sup>	0	10.5 <sup>b</sup>

Conditions: 1 g resin, bed volume 2 ml; flow rate 8 ml h<sup>-1</sup>; <sup>a</sup> 2 M HCl; <sup>b</sup> 1 M KCN; eluent volume for 100% recovery of Pd(II) or Au(III) = 12 ml (2 M HCl or 1 M KCN); <sup>c</sup>  $\mu = 1$  mol/l KCl (initial solutions).

from Pd(II) and/or Pt(IV) by anion exchange. The elution conditions (2 M HCl, 1 M KCN) do not compromise the stability of the resin. The saturation sorption capacities at pH 6 (0.89 mmol Au and 0.84 mmol Pd/g dry resin) correspond to about 60% of the theoretical capacity (1.49 mmol/g based on elemental analysis); this may indicate that some chelating groups are not available for chelation because they are placed in a less favourable microenvironment for metal ion solution.

#### ACKNOWLEDGEMENTS

We thank the Italian Ministry of Education and CNR (Rome) for financial support and Miss Tatiana Bobbo for technical assistance.

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