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Solvent Extraction of Palladium(II) and Platinum(IV) with *N,N*-Dioctylsuccinamic Acid from Aqueous Chloride Media

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N,N-Dioctylsuccinamic acid was synthesized to examine the selectivity for various metals in extractions from hydrochloric acid. It was found to be highly selective for palladium(II), platinum(IV), and mercury(II) over other base metals including copper(II), nickel(II), cobalt(II), zinc(II), iron(III), aluminum(III), and gallium(III). A quantitative study was conducted on the extraction equilibria of palladium(II) and platinum(IV) from aqueous chloride media with *N,N*-dioctylsuccinamic acid in toluene, together with measurement of the apparent molecular weight of the extractant. It was elucidated that the extractant (HR) dimerizes in toluene and that palladium(II) and platinum(IV) are extracted according to the following reactions:

$$\mathrm{PdCl_4^{2-}} + \overline{\mathrm{H_2R_2}} \overset{K_{\mathrm{e,Pd}}}{\rightleftharpoons} \overline{\mathrm{PdR_2}} + 2\mathrm{H^+} + 4\mathrm{Cl^-}$$

$$\mathrm{PtCl_6^{2-}} + \overline{\mathrm{H_2R_2}} \overset{K_{\mathrm{e,Pt}}}{\rightleftharpoons} \overline{\mathrm{PtCl_4{\cdot}2HR}} + 2\mathrm{Cl^-}$$

The extraction equilibrium constants of palladium(II) and platinum(IV) with the extractant were evaluated as follows: $K_{\mathrm{e,Pd}}=0.11\pm0.03\ (\mathrm{mol\cdot dm^{-3}})^5$ and $K_{\mathrm{e,Pt}}=27.7\pm3.7\ \mathrm{mol\cdot dm^{-3}}$, respectively.

With the rapid advance of the high-technology industries, precious metals such as gold, silver and the platinum group metals are indispensable as raw materials of catalysts, alloy materials of electronic devices and so on. Since these metals coexist with common metals and/or other metals of the same family in feed materials, a highly skilled technique is required to separate and refine the individual precious metal.

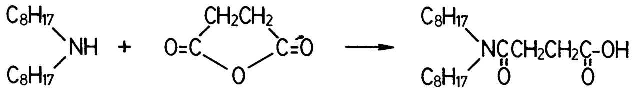
However, conventional refining processes for precious metals are commonly based on the complicated selective precipitation method which needs much energy and labor. Therefore, it is importnat to develop an alternative refining process from the view points of both saving energy and increasing the separation efficiency.

Among the alternative processes, it is considered that the solvent extraction is exceedingly promising as also is ion exchange. The development of the extractants with high selectivity for individual metals has a vital significance for the commercial application of the solvent extraction technique to the refining of precious metals.

Following the previous study on the extraction with *N,N*-dioctylglycine,[1,2] the authors synthesized *N,N*-dioctylsuccinamic acid and, firstly investigated its qualitative extraction capability for various metals from hydrochloric acid. Subsequently, we conducted a quantitative study on the extraction of palladium(II) and platinum(IV) from aqueous chloride media, together with the measurement of apparent molecular weight of the extractant in toluene, so as to elucidate the extraction stoichiometry and to evaluate the extraction equilibrium constants.

Experimental

Reagents. *N,N*-Dioctylsuccinamic acid (henceforth abbreviated, $2\mathrm{C_8NC_2CA}$, and denoted by HR) was synthesized from dioctylamine and succinic anhydride by a conventional method according to the following reaction:



To a benzene solution (300 cm^3) of dioctylamine (58 g, 0.24 mol) was added succinic anhydride (24 g, 0.24 mol). The mixture was stirred and refluxed at 353 K for 1 h under a nitrogen atmosphere. After washing the pale yellow organic solution in turn with 1 mol·dm^{-3} sodium hydroxide solution, 2 mol·dm^{-3} sulfuric acid solution, and deionized water several times, the benzene was evaporated from the solution and the product dried in vacuo. The yield of the product was 87.6%. The purity of the product was found to be 96.1% by neutralization titration with alcoholic potash using phenolphthalein as indicator. The identification of the product was carried out by infrared and ^{1}H NMR spectroscopies. The elemental analysis of the product was obtained as follows; Found: C, 69.26; H, 11.53; N, 3.90%. Calcd for $\mathrm{C_{20}H_{39}O_3N}$: C, 70.34; H, 11.51; N, 4.10%.

The organic solution was prepared by dissolving $2\mathrm{C_8NC_2CA}$ in toluene of reagent grade to a required concentration gravimetrically. The aqueous solutions for selectivity study of $2\mathrm{C_8NC_2CA}$ were prepared by dissolving chlorides of the corresponding metals of reagent grade in hydrochloric acid. The initial metal concentrations of these aqueous solutions were about 25 ppm. For the quantitative studies, the aqueous solution of palladium(II) was prepared by dissolving palladium(II) chloride in an aqueous mixture of 1.0 mol·dm^{-3} hydrochloric acid and 1.0 mol·dm^{-3} sodium chloride, while the solution of platinum(IV) was prepared by dissolving hydrogen hexachloroplatinate(IV) hexahydrate in the mixture of 1.0 mol·dm^{-3} hydrochloric acid and

1.0 mol·dm^{-3} lithium chloride solution, to adjust pH and chloride ion concentration. Intitial concentrations of palladium(II) and platinum(IV) were 25 ppm (0.23 mmol·dm^{-3}) and 100 ppm (0.51 mmol·dm^{-3}), respectively.

Measurement of Apparent Molecular Weight of $2C_8NC_2CA$. Apparent molecular weight of $2C_8NC_2CA$ in toluene was measured with a Corona model 117 vapor-phase osmometer, using benzil as a standard material.

Extraction Equilibria. In the extractions of all metals except palladium(II) and platinum(IV), equal volumes (20 cm^3) of aqueous and organic phases were vigorously shaken for over 24 h in a separatory funnel using an Iwaki's type V-DN mechanical shaker in an air bath maintained at 303 K. In the extractions of palladium(II) and platinum(IV), the phases were shaken for over 72 h. Equilibrium was ensured in a preliminary experiment.

After equilibration, the phases were separated and analyzed for metal concentration in the aqueous phase by a Nippon Jarrel-Ash model AA-782 atomic absorption spectrophotometer. The metal concentrations in the organic phase were calculated from the mass balance of the metal contents in the aqueous phase before and after the equilibria. At pH>1.0, pH of the aqueous phase was measured using a TOA model HM-20E pH meter. At pH<1.0, the activity of hydrogen ion in the aqueous solution was calculated from the hydrogen ion concentration measured by titration and the activity coefficient of the hydrogen ion.[3,4] The chloride ion activity was calculated from the concentration of the chloride ion and the activity coefficients of the aqueous mixture of hydrochloride acid and sodium chloride or lithium chloride.[4]

Spectroscopic Studies. The sample solution of the palladium(II) or platinum(IV) complexes with $2C_8NC_2CA$ was prepared by the following procedure: (1) the toluene solution containing $2C_8NC_2CA$ and the aqueous solution containing each metal ion were vigorously shaken in the same manner as mentioned before and the organic solution was dried with anhydrous sodium sulfate after phase separation, (2) the toluene was completely evaporated from the solution and dried in vacuo, and (3) the viscous liquid was dissolved in $CDCl_3$.

Infrared spectra of $2C_8NC_2CA$ and its metal complexes in the $CDCl_3$ solution were recorded on a JASCO model A-100 spectrometer, using 0.05 mm CaF_2 IR cells. ^{1}H NMR spectra in $CDCl_3$ were obtained on a JEOL model JNM-GX270 FT-NMR spectrometer.

Results and Discussion

Dimerization of the Extractant. It is considered that $2C_8NC_2CA$ dimerizes in a nonpolar diluent such as toluene as well as other carboxylic acids.

The dimerization equilibrium of the extractant in the organic phase is expressed as follows:

$$2\overline{\mathrm{HR}} \overset{K_d}{\rightleftharpoons} \overline{\mathrm{H_2R_2}} \qquad (1)$$

From the above equation, the dimerization constant, K_d, and the number-averaged aggregation number, m, are given by the following equations:

$$K_d = [\overline{\mathrm{H_2R_2}}]/[\overline{\mathrm{HR}}]^2 = (C_{\overline{\mathrm{HR}}} - C^*)/(2C^* - C_{\overline{\mathrm{HR}}})^2 \qquad (2)$$

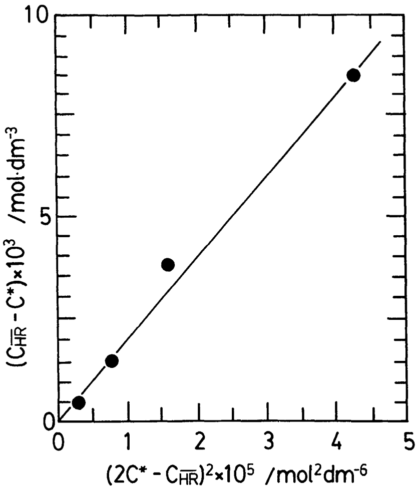


Fig. 1. Determination of Dimerization constant of $2C_8NC_2CA$ in toluene.

$$m = C_{\overline{\mathrm{HR}}}/C^* \qquad (3)$$

where $C_{\overline{\mathrm{HR}}}(=2[\overline{\mathrm{H_2R_2}}]+[\overline{\mathrm{HR}}])$ and $C^*(=[\overline{\mathrm{H_2R_2}}]+[\overline{\mathrm{HR}}])$ are the analytical concentration of $2C_8NC_2CA$ and the total concentration of the monomeric and dimeric species in toluene measured experimentally, respectively and the bar superscript denotes the organic phase.

Figure 1 shows the relationship between $(C_{\overline{\mathrm{HR}}}-C^*)$ and $(2C^*-C_{\overline{\mathrm{HR}}})^2$ according to Eq. 2. From the linear relationship, the dimerization constant was obtained as $K_d=200\pm36$ dm^3·mol^{-1}, and the number-averaged aggregation number was $m=1.54\pm0.08$ in the concentration region from $C_{\overline{\mathrm{HR}}}=0.002$ to 0.03 mol·dm^{-3}. It can be concluded that $2C_8NC_2CA$ is apt to partially dimerize in toluene.

Selectivity of $2C_8NC_2CA$ to Various Metals. Prior to the quantitative investigation on the extractions of palladium(II) and platinum(IV), the qualitative study on the extractions of palladium(II), platinum(IV), mercury(II), copper(II), nickel(II), cobalt(II), zinc(II), iron(III), aluminum(III), and gallium(III) from hydrochloric acid with 0.01 mol·dm^{-3} $2C_8NC_2CA$ in toluene was undertaken to examine the selectivity of the extractant for these metals.

As shown in Fig. 2, over the hydrochloric acid concentration region from 0.005 to 0.1 mol·dm^{-3}, palladium(II) was completely extracted, whereas only about 70% of the platinum(IV) was extracted. Above 0.1 mol·dm^{-3} hydrochloric acid, the percent extraction linearly decreased with increasing concentration of hydrochloric acid. The percent extraction of mercury(II) increased with increasing concentration of hydrochloric acid, and after passing through a maximum, gradually decreased. Gallium(III) was extracted above 3 mol·dm^{-3} hydrochloric acid.

Copper(II), nickel(II), cobalt(II), zinc(II), iron(III), and aluminum(III) were scarcely extracted at all over the hydrochloric acid concentration region from 0.01

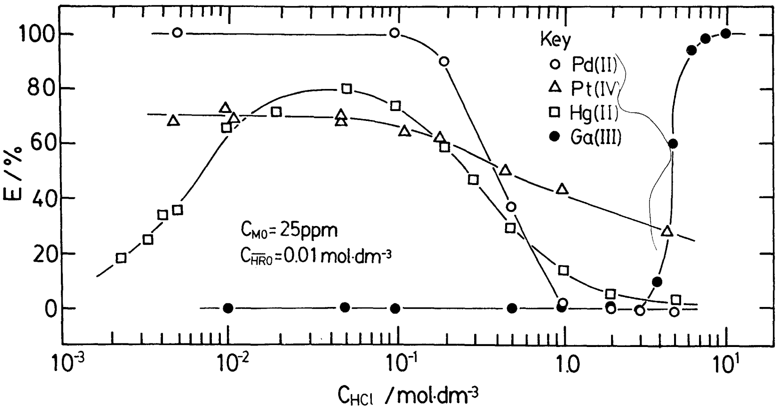


Fig. 2. Percent extraction of metals from hydrochloric acid.

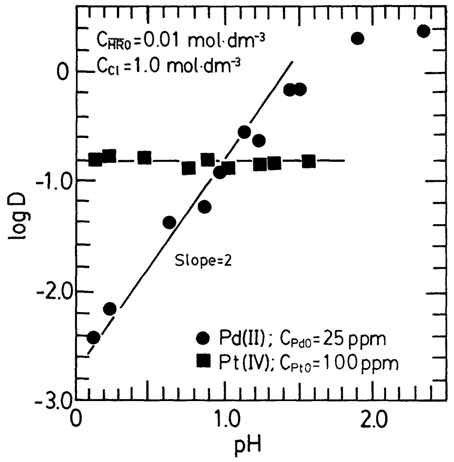


Fig. 3. Effect of pH of aqueous solution on distribution ratio of metal.

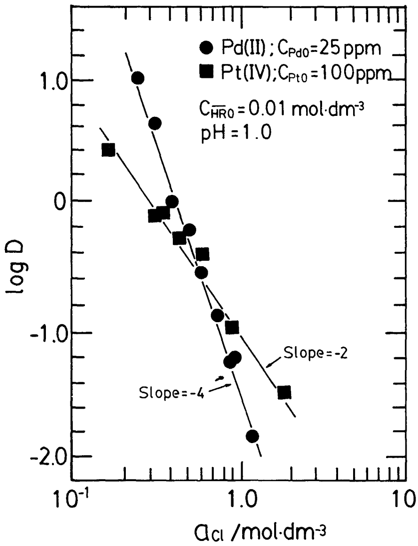


Fig. 4. Effect of chloride ion activity on distribution ratio of metal.

to 10 mol·dm^{-3}.

Extraction Equilibria of Palladium(II) and Platinum(IV). Extraction equilibria of palladium(II) and platinum(IV) from aqueous chloride media was studied by examining the effect of the concentration of each reactant species on the distribution ratio of the metals, to elucidate the stoichiometric relation of the extraction reactions and to evaluate the extraction equilibrium constants. Here, the distribution ratio of metal, *D*, was calculated by the ratio between the metal concentration in the organic phase and that in the aqueous phase.

Figure 3 shows the effect of the pH of the aqueous phase at equilibrium on the distribution ratio of each metal at the constant concentrations of chloride ion, C_{Cl}, and the extractant, $C_{\overline{HR}0}$. In Fig. 3, the plotted points for palladium(II) appear to lie on a straight line with a slope of 2 at low pH (pH<2) and tend to approach a constant value at high pH. This suggests that the extraction of palladium(II) has inversely second order dependency on the hydrogen ion activity at low pH. However, at high pH, a precipitate of the palladium(II) complex with $2C_8NC_2CA$ was found to be formed in the organic phase and at the interface between the organic and aqueous phases. This is due to the low solubility of the palladium(II)–$2C_8NC_2CA$ complex in toluene. Therefore, the experiments on the extraction of palladium(II) were carried out hereafter in the low pH range (pH<2.0).

On the other hand, the plotted points for platinum(IV) are independent of pH over the whole pH range, which suggests that the extraction of platinum(IV) has zero order dependency on the hydrogen ion activity.

Figure 4 shows the effect of the chloride ion activity of the aqueous phase, a_{Cl}, on the distribution ratio at constant concentration of the extractant and pH. The plotted points for palladium(II) lie on a straight line with the slope of −4, suggesting that the extraction of palladium(II) shows inversely fourth order dependen-

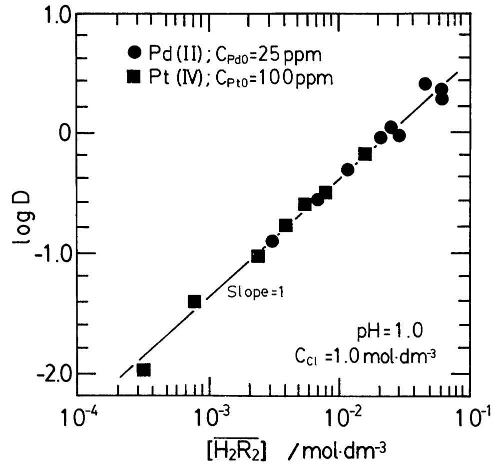


Fig. 5. Effect of concentration of dimeric species of extraction on distribution ratio of metal.

cy on a_{Cl}. On the other hand, the plotted points for platinum(IV) lie on a straight line with the slope of −2, suggesting that the extraction of platinum(IV) shows inversely second order dependency on a_{Cl}.

Figure 5 shows the effect of the concentration of the dimeric species of the extractant in the organic phase, $[\overline{H_2R_2}]$, which was calculated from Eq. 2 and K_d evaluated earlier, on the distribution ratio at the constant concentration of chloride ion and pH. The plotted points for both metals lie on a single straight line with the slope of unity over the whole experimental range of $[\overline{H_2R_2}]$. This suggests that the extraction of both metals shows first order dependency on $[\overline{H_2R_2}]$.

From the results described above, it can be considered that palladium(II) and platinum(IV) are extracted according to the following extraction reactions:

$$PdCl_4^{2-} + \overline{H_2R_2} \overset{K_{e,Pd}}{\rightleftharpoons} \overline{PdR_2} + 2H^+ + 4Cl^- \qquad (4)$$

$$PtCl_6^{2-} + \overline{H_2R_2} \overset{K_{e,Pt}}{\rightleftharpoons} \overline{PtCl_4 \cdot 2HR} + 2Cl^- \qquad (5)$$

The extraction equilibrium constants, $K_{e,Pd}$ and $K_{e,Pt}$, are expressed by:

$$K_{e,Pd} = \frac{[\overline{PdR_2}] \cdot a_H{}^2 \cdot a_{Cl}{}^4}{[PdCl_4^{2-}][\overline{H_2R_2}]} \qquad (6)$$

$$K_{e,Pt} = \frac{[\overline{PtCl_4 \cdot 2HR}] \cdot a_{Cl}{}^2}{[PtCl_6^{2-}][\overline{H_2R_2}]} \qquad (7)$$

where $[PdCl_4^{2-}]$ and $[PtCl_6^{2-}]$ are the concentrations of chloro-complex of palladium(II) and platinum(IV) expressed as:

$$[PdCl_4^{2-}] = \frac{\beta_4 a_{Cl}{}^4}{1 + \sum_{i=1}^{4} \beta_i a_{Cl}{}^i} C_{Pd} \qquad (8)$$

$$[PtCl_6^{2-}] = \frac{\beta_6 a_{Cl}{}^6}{1 + \sum_{i=1}^{6} \beta_i a_{Cl}{}^i} C_{Pt} \qquad (9)$$

where C_{Pd} and C_{Pt} are the total concentrations of palladium(II) and platinum(IV) in the aqueous phase, respectively, and β_i is the stability constant of i-th chloro-complex of palladium(II) and platinum(IV).[5)]

Since the chloro-complexes of palladium(II) exist as $PdCl_4^{2-}$ and the complexes of platinum(IV) as and $PtCl_6^{2-}$ in the aqueous phase under the present experimental conditions ($a_{Cl} > 0.2$ mol·dm^{-3}), it is considered that the total concentrations of palladium(II) and platinum(IV) in the aqueous phase is nearly equal to the concentration of $PdCl_4^{2-}$ and $PtCl_6^{2-}$, respectively. Therefore, the following equations are obtained for both metals:

$$K_{e,Pd} = \frac{[\overline{PdR_2}] \cdot a_H{}^2 \cdot a_{Cl}{}^4}{C_{Pd} \cdot [\overline{H_2R_2}]} = D \frac{a_H{}^2 \cdot a_{Cl}{}^4}{[\overline{H_2R_2}]} \qquad (10)$$

$$K_{e,Pt} = \frac{[\overline{PtCl_4 \cdot 2HR}] \cdot a_{Cl}{}^2}{C_{Pt} \cdot [\overline{H_2R_2}]} = D \frac{a_{Cl}{}^2}{[\overline{H_2R_2}]} \qquad (11)$$

Eqs. 10 and 11 can be rearranged as follows:

$$\log D = \log K_{e,Pd} + \log \frac{[\overline{H_2R_2}]}{a_H{}^2 \cdot a_{Cl}{}^4} \qquad (12)$$

$$\log D = \log K_{e,Pt} + \log \frac{[\overline{H_2R_2}]}{a_{Cl}{}^2} \qquad (13)$$

Eqs. 12 and 13 can explain all the dependencies of the concentration of each species on D obtained experimentally.

In order to evaluate the extraction equilibrium constants of palladium(II) and platinum(IV), $K_{e,Pd}$ and $K_{e,Pt}$, all the experimental results were plotted according to Eqs. 12 and 13 as shown in Fig. 6. The plots are lying on straight lines with a slope of unity for each metal as expected. The extraction equilibrium constants were obtained as $K_{e,Pd}=0.11\pm0.03$ (mol·dm^{-3})^5 for palladium(II) and as $K_{e,Pt}=27.7\pm3.7$ mol·dm^{-3} for platinum(IV) from the intersections of the straight lines and the ordinates in Fig. 6, respectively.

Consequently, it can be found that $2C_8NC_2CA$ plays two different kinds of role as an extractant: a chelate extractant for palladium(II) and a solvating extractant for platinum(IV), similarly as observed in the extraction with *N*,*N*-dioctylglycine.[1,2)]

Spectroscopic Studies of $2C_8NC_2CA$ and Its Metal Complexes. Figure 7 compares the infrared spectra of the palladium(II) and platinum(IV) complexes with that of the free $2C_8NC_2CA$. The spectrum of the platinum(IV) complex(b) resembles that of the free reagent(a). On the other hand, the spectrum of the palladium(II) complex(c) differs significantly from those of the platinum(IV) complex and the free reagent in the region of the C=O stretching bands at 1710 cm^{-1}

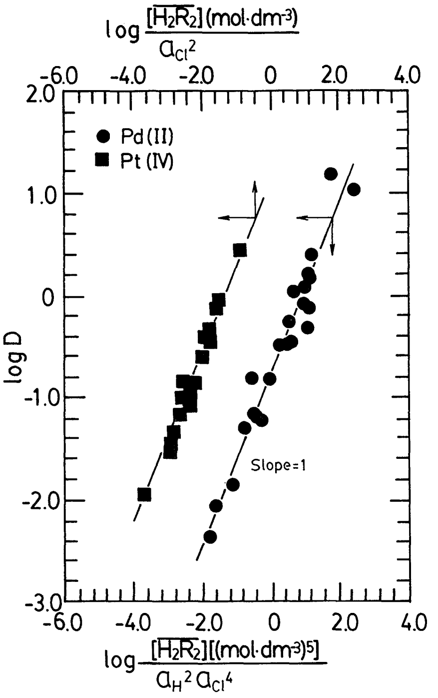


Fig. 6. Plot of all the experimental data for the extraction of palladium(II) and platinum(IV) based on Eqs. 12 and 13.

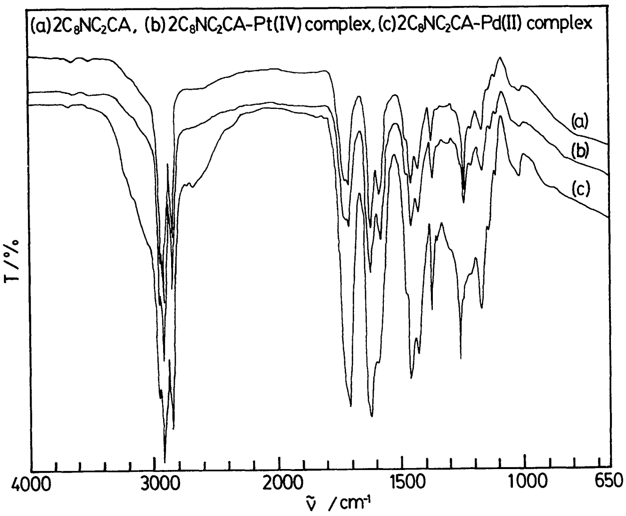


Fig. 7. Infrared spectra of free reagent and the palladium(II) and platinum(IV) complexes.

(carbonyl group of amide) and 1630 cm^{-1} (carboxyl group). These absorption bands are assigned to the bidentate (chelated) succinamic acid group.⁶⁾

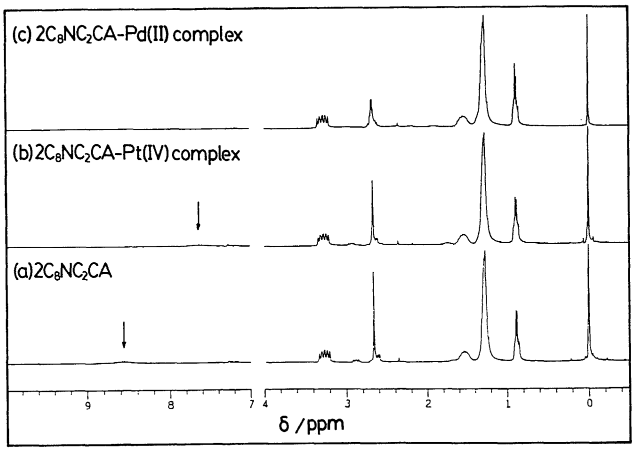
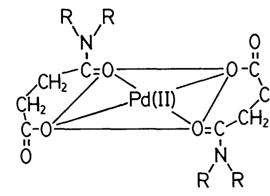
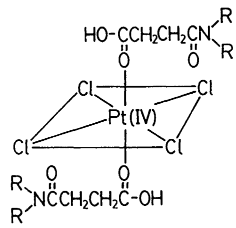


Fig. 8. ^{1}H NMR spectra of free reagent and the palladium(II) and platinum(IV) complexes.

Figure 8 shows the ^{1}H NMR spectra of $2C_8NC_2CA$ and its metal complexes. The spectrum of the platinum(IV) complex(b) is similar to that of the free reagent(a), except for 1.0 ppm shift of the carboxylic OH signal toward higher magnetic field (from 8.6 ppm to 7.6 ppm). While in the spectrum of palladium(II) complex(c), the signal of carboxylic OH disappeared and the signal of succinyl protons at 2.7 ppm becomes broad.

These facts support the view that palladium(II) is extracted as a chelate complex of the type, PdR_2, and platinum(IV) as a solvation complex of the type, $PtCl_4 \cdot 2HR$ as shown below, in agreement with the conclusion obtained in the experiments of the distribution equilibria.





Comparison of the Extraction Mechanisms between $2C_8NC_2CA$ and *N*,*N*-Dioctylglycine. The authors reported previously that palladium(II) and platinum(IV) are extracted from aqueous chloride media with *N*,*N*-dioctylglycine (abbreviated as $2C_8$gly) in toluene in a similar manner to the extraction reaction with $2C_8NC_2CA$ described by Eqs. 4 and 5. The extraction equilibrium constants of palladium(II) and platinum(IV) with the extractant were evaluated as follows: $K_{e,Pd}=220\ (\mathrm{mol \cdot dm^{-3}})^5$ and $K_{e,Pt}=630\ \mathrm{mol \cdot dm^{-3}}$, respectively.¹·²⁾

The extraction equilibrium constants of palladium(II) and platinum(IV) with $2C_8NC_2CA$ is 2000 times and 23 times smaller than those of $2C_8$gly, respectively. However, this also suggests that the stripping of the metals from $2C_8NC_2CA$ is easy compared with that from $2C_8$gly.

Conclusion

From the qualitative and quantitative studies on the extraction equilibria of palladium(II), platinum(IV), and base metals with *N,N*-dioctylsuccinamic acid in toluene from aqueous chloride media, the following information was obtained:

(1) *N,N*-Dioctylsuccinamic acid partially dimerizes in toluene and the dimerization constant was evaluated.

(2) *N,N*-Dioctylsuccinamic acid was found to be selective to palladium(II), platinum(IV), and mercury(II) over base metals such as copper(II), nickel(II), and gallium(III).

(3) The extracted species of palladium(II) and platinum(IV) with *N,N*-dioctylsuccinamic acid are PdR_2 and $PtCl_4\cdot 2HR$; the equilibrium constants for these metals were evaluated.

(4) The spectroscopic studies also supported the view that the extractant acts differently for palladium(II) and platinum(IV), giving rise to a chelate complex and a solvation complex, respectively.

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