

# Studies on Syntheses and Properties of Chelating Resins Based on Chitosan

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## SYNOPSIS

Chelating resins have some good adsorption properties for some metal ions, especially for several noble metal ions. Thus to retrieve rare metals using chelating resins is always an interesting project for chemistry researchers. In this study we synthesized a series of chelating resins based on chitosan and investigated adsorbing capacities, adsorption rates, and adsorption selectivities for Ag(I), Au(III), Pd(II), Pt(IV), Cu(II), Hg(II), and Zn(II). The results indicate that the resins have remarkable adsorbing capacities and adsorption rates for four noble metal ions and Hg(II). For instance, one of the resins adsorbs Au(III) and the adsorbing capacity is up to 7.11 mmol/g. However, the adsorbing capacities of the resins for Cu(II) and Zn(II) are much less than for the noble metal ions. Finally, x-ray photoelectron spectroscopy studies of a chelating resin and its metal chelates were made. The result reveals that the basis of the chelations is a chemical process. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

There are numerous reports about syntheses and properties of chelating resins.<sup>1-7</sup> Various types of chelating resins such as polyethylene polyamine, polythioether, dithiocarboxylic acid, mercapto, mercaptoamino, thiourea, and heterocycle have been synthesized. Mgasodova et al.<sup>6</sup> reported the linkage of imidazole to a special solid support of polymer, obtaining a chelating resin with adsorbing capacity of 660 mg/g for Au(III). Zolotov et al.<sup>7</sup> used a simple reaction to synthesize a polythioether type resin that had a adsorption selectivity to platinum family elements in very dilute solutions of metal ions. Yuwu et al.<sup>8</sup> synthesized several mercapto amine chelating resins through reacting chloromethyl thiirane (CT) with polyethylene polyamine. The adsorbing capacities of these resins for noble metal ions are considerable. Because chelating resins have excellent adsorption properties for the valuable metal ions, obtaining highly efficient chelating resins in a simple and economical manner is desirable.

Previous reports reveal that resins containing function groups of sulfur and nitrogen have extraordinary adsorption properties. It is also known that chitosan is a derivative of deacetylated chitin that exists extensively in the natural world.<sup>9</sup> Therefore, in this study chitosan was reacted with CT to synthesize a series of crosslinked chelating resins containing amino and mercapto groups, and the adsorption and the x-ray photoelectron spectroscopy (XPS) properties of resins was investigated. The results are notable.

## EXPERIMENTAL

### Preparation of Materials

Chitosan was prepared from chitin using the method described by Mima et al.<sup>10</sup> CT was prepared, following the method of Tabushi,<sup>11</sup> in yields of 60%, b.p. 60–61°C (45 mmHg);  $n_D$ , 1.5222. *N,N*-Diethylaminomethyl oxirane (ON) was prepared following the method of Gilman<sup>12</sup> through the reaction of epoxy chloropropane and diethylamine, in yields of 65%,  $n_D$ , 1.4360. *N,N*-Diethylaminomethyl thiirane (SN) was prepared, using the Stewart method,<sup>13</sup> by the reaction of CT and diethylamine, in yields of 30%,  $n_D$ , 1.4850.

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**Table I** Syntheses of Chelating Resins

Resins	Chitosan (g)	MH <sub>2</sub> (mol)	CT		NH <sub>2</sub> : CT (mol)	Yields (g)	Analyses (%)	
			g	mol			S	N
PCS <sub>1</sub>	4.85	0.03	1.65	0.015	1 : 0.5	3.45	1.26	6.89
PCS <sub>2</sub>	4.85	0.03	3.30	0.030	1 : 1	4.90	4.87	6.46
PCS <sub>3</sub>	4.85	0.03	6.60	0.060	1 : 2	5.05	8.06	6.05
PCS <sub>4</sub>	4.85	0.03	16.28	0.150	1 : 5	6.02	16.76	3.71
PCS <sub>5</sub>	4.85	0.03	33.00	0.300	1 : 10	12.05	24.20	2.55

### Syntheses of PCS Resins

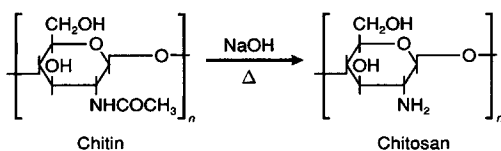
Chitosan (4.83 g, 0.03 mol—NH<sub>2</sub>) was placed in a reaction vessel with a solution of water and dioxane. CT (1.62 g, 0.015 mol) was added dropwise to the reaction vessel within 2 h while heating (75°C) and stirring. Five percent sodium hydrate was added to the mixture, and the reaction continued for 14 h. The product was then washed in turn by 2 mol/L of hydrochloric acid, 2% acetic acid, 1.0 mol/L of sodium hydrate, and distilled water. A light yellow powder resin (PCS<sub>1</sub>) was obtained after drying for 6 h at a reduced pressure (60°C, 5 mmHg). In the same manner, by changing the ratios of chitosan to CT, a series of similar resins PCS<sub>2</sub>, PCS<sub>3</sub>, PCS<sub>4</sub>, and PCS<sub>5</sub> were obtained. The results are shown in Table I.

### Syntheses of PCSSN and PCOON

Chitosan (16 g) and CT (2.2 g) were mixed in a solution of water and dioxane. Using the above technique, a crosslinked product was obtained (analysis S, 1.95%; N, 7.38%). After the reaction of this product with SN in the presence of sodium hydrate, the resin PCSSN was obtained (analysis S, 12.62%; N, 7.35%). By substituting epoxy chloropropane and ON for CT and SN, we synthesized the resin PCOON (analysis N, 8.12%).

### Examinations of Adsorption Properties

The adsorption properties were examined using a static method.

**Scheme 1.**

### Adsorbing Capacities for Ag(I)

Resin, 0.25 g, was placed in a small conical flask containing 25.0 mL AgNO<sub>3</sub> solution (0.1 mol/L). The flask was wrapped in black paper to exclude all light. After being motionless for 22 h, the mixture was vibrated for 2 h and then filtrated. The concentration of Ag(I) in the solution was measured using the Volhard method and the adsorbing capacities were calculated.

### Adsorbing Capacities for Au(III), Pd(II), Pt(IV)

Twenty-five milligrams of resin, 25 mL of metal ion (1 mg/mL), and 2 mol/L of hydrochloric acid solution were mixed in a conical flask, and then subjected to the same analysis as above. The concentration of the metal ion was measured using the Isoionic Emission Spectrum method (ICP).

### Adsorbing Capacities for Hg(II), Cu(II), Zn(II)

Sixty milligrams of resin and 50 mL of metal ion solution (0.025 mol/L) were mixed and again analyzed as above. The concentration of metal ions were measured by EDTA titration.

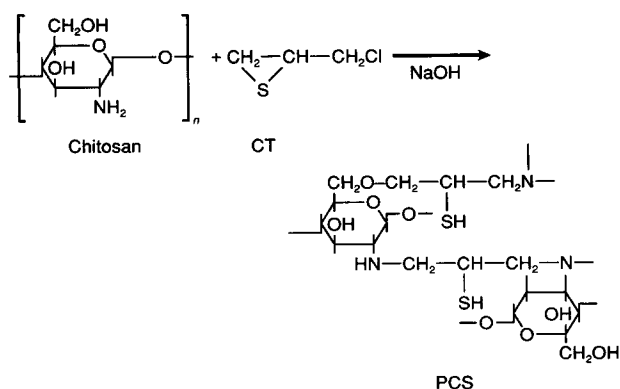
### Adsorption Rates for Au(III), Pd(II), Pt(IV)

Twenty-five milligrams of resin and 25.0 mL of metal ion solution (0.1 mg/mL) were mixed. The concentration of metal ions before and after adsorption were measured using the procedure described.

## RESULTS AND DISCUSSION

### Syntheses of Chelating Resins

Chitosan is the product of deacetylated chitin (Scheme 1). As chitosan is soluble in acids, it must



be crosslinked to be used as a chelating resin. Crosslink agents such as epoxy chloropropane<sup>14</sup> and cyanuric chloride<sup>15</sup> were studied previously. We know that primary amino groups exist in each chain segment of chitosan, and they are able to react with thiirane groups. In the presence of sodium hydrate, chitosan reacts with and forms crosslinked chelating resins containing mercapto and amino groups. The expected reaction is shown in Scheme 2.

To investigate the influence of the reactants' molar ratios on the products and their properties, we changed the molar ratios in chitosan of the  $\text{—NH}_2$  groups to CT, with ratios of 1 : 0.5, 1 : 1, 1 : 2, 1 : 5, and 1 : 10, respectively, and obtained the resins shown in Table I.

The results indicated that when the amount of chitosan was fixed, the yields of the products increased with the increment in the amount of CT in the reaction, as did the percentage of sulfur in the resins. The infrared spectrogram of PCS<sub>5</sub> showed the existence of mercapto groups ( $2400\text{ cm}^{-1}$ ), and also the weak adsorption peak of thioether bonds ( $826$  and  $780\text{ cm}^{-1}$ ). The inference was that CT was joined to chitosan by graft polymerization. The per-

centage of chlorine in the resins was  $< 1.9\%$ , indicating that the dehydrochlorination between chitosan and CT was nearly completed. The adsorbing capacities of these resins are shown in Table II.

The adsorbing capacities of the PCS resins for Ag(I) were higher than that of chitosan. In acidic solution (1 mol/L  $\text{HNO}_3$ ), the adsorbing capacity of chitosan was close to zero, whereas PCS<sub>5</sub> had an adsorbing capacity of 5.3 mmol/g. Whether in neutral or acidic solutions, the adsorbing capacities increased in an orderly fashion from PCS<sub>1</sub> to PCS<sub>5</sub>, in which the sulfur content correspondingly increased. In the neutral solution there were no obvious differences in the adsorbing capacities of different resins because both the amino and mercapto groups contributed to adsorbing capacities. However, in acidic solutions the amino groups became quaternary salt and lost their adsorbing ability for Ag(I). The mercapto groups played a dominant role in these adsorptions. It is clear that the adsorbing capacities increased with the sulfur content of the resins.

Table II showed that in general the resins had increasing adsorbing capacities from PCS<sub>1</sub> to PCS<sub>5</sub> for Au(III), Pd(II), and Pt(IV). The S content of the resins increased from PCS<sub>1</sub> to PCS<sub>5</sub>, whereas the N content decreased. Groups containing sulfur seem to give more to the adsorbing capacities than those of other groups. The resins have considerable adsorbing capacities for Hg(II), but have less adsorbing capacities for Cu(II) or Zn(II). Generally these adsorbing capacities decreased from PCS<sub>1</sub> to PCS<sub>5</sub> for each of the metal ions. This shows that coordinate atoms of the chelating resins have different adsorbing abilities for the different metal ions.

### Adsorption Rates

To examine the retrieving efficiency of the resins, some very dilute solutions of metal ions were made

**Table II** Adsorbing Capacities of Resins (mmol/g)

Resins	Ag (I)		2 mol/L HCl			pH 5.6		
	pH 7	$\text{NHO}_3$	Au (III)	Pd (II)	Pt (IV)	Hg (II)	Cu (II)	Zn (II)
PCS <sub>1</sub>	3.21	0.86	0.95	0.87	0.39	4.60	2.05	1.26
PCS <sub>2</sub>	3.12	1.58	2.32	1.90	1.53	4.70	2.19	1.06
PCS <sub>3</sub>	3.37	2.16	3.54	2.11	1.54	3.97	1.97	1.03
PCS <sub>4</sub>	3.64	3.94	4.72	2.24	1.35	3.10	1.46	0.67
PCS <sub>5</sub>	4.46	5.31	4.86	3.51	1.87	2.61	0.88	0.10
Chitosan	2.98	0.05	1.28	0.96	0.49	3.37	1.46	1.30

**Table III Adsorption Selectivities of PCS<sub>5</sub> (mg/mL)**

Mixtures	Au (III) – Pd (II)		Au(III) – Pt (IV)		Pd (II)	– Pt (IV)
C <sub>1A</sub> , C <sub>1B</sub>	0.554	0.549	0.554	0.486	0.549	0.486
C <sub>2A</sub> , C <sub>2B</sub>	0.306	0.363	0.206	0.339	0.184	0.370
K	1.6		7.7		6.3	

The medium of the solution is 2 mol/L HCl.

[Au(III), Pd(II), Pt(IV): 0.1 mg/mL, Ag(I): 0.01 mol/L] and then PCS<sub>5</sub> resin was used to adsorb the metal ions. After measuring concentrations of the metal ions, the adsorption rates were calculated using the equation  $R = (C_1 - C_2)/C_1$ , where  $R$  was the adsorption rate, and  $C_1$  and  $C_2$  were the concentrations of the metal ions in solutions before and after adsorption. The adsorption rates calculated were 100, 99.9, 94.5, and 89.2% for Ag(I), Au(III), Pd(II), and Pt(IV), respectively.

### Adsorption Selectivities

Three groups of mixed solutions of metal ions [Au(III)-Pd(II), Au(III)-Pt(IV), Pd(II)-Pt(IV)] were prepared and PCS<sub>5</sub> resin was used to examine the adsorption selectivities. The separating factor ( $K$ ) was calculated using the equation:

$$K = (C_{1A} - C_{2A}) \times C_{2B} / (C_{1B} - C_{2B}) \times C_{2A}$$

where  $C_{1A}$  and  $C_{2A}$  stand for the concentrations of metal ion A before and after adsorption, and  $C_{1B}$  and  $C_{2B}$  stand for the concentrations of metal ion B again before and after adsorption. The results are shown in Table III. From these separating factors it can be seen that the resins have a special adsorbing priority to a certain ion in a certain solution.

### Adsorption Speed and Repeat Adsorption

The adsorption speed was examined using PCS<sub>5</sub> in a neutral solution of AgNO<sub>3</sub> with a different adsorption time. The result is shown in Table IV.

**Table IV Adsorption Capacities at Different Times (mmol/g)**

Time (h)	1	3	5	12	24	48
Capacities	2.86	3.50	3.77	4.25	4.60	4.60

The adsorbing capacities increase with time for the first 24 h. To examine the stability of the resins, we tested the repeatability of the adsorbing capacities of PCS<sub>5</sub> for Ag(I). When adsorption was finished, the metal ions were then extricated from the resins. After treating the resin, the measurement of adsorbing capacity was repeated. The results showed little variation in the adsorbing capacities over the four measurements.

### Syntheses and Properties of Resins Derived from PCS

ON and SN contain tertiary amino groups and epoxy and thiirane groups, respectively. They were expected to react with chitosan, so the lightly cross-linked chitosan was taken and reacted with ON and SN, synthesizing two kinds of chelating resins, namely PCOON and PCSSN.

[analyses S, 12.62% (PCSSN); N, 7.35% (PCSSN); 8.02% (PCOON)]. The adsorbing capacities shown in Table V are satisfactory. The Au(III) adsorbing capacity of 7.11 mmol/g is highly notable.

### XPS of Metal Chelates

PCS<sub>5</sub>, 0.5 g, and 100 mL Au(III) solution (1.0 mg/mL) were mixed with 2 mol/L HCl medium. After adsorption and filtration, the resin was dried out by heating in a vacuum. The same adsorption procedures were repeated by substituting Pd(II) and Pt(IV) for Au(III). The electron binding energies (EBE) of the resin and its metal chelates were measured on a Kratos XSAM 800 photoelectron spectroscopy Instrument. The results are shown in Table VI.

**Table V Adsorbing Capacities of PCOON and PCSSN (mmol/g)**

Resins	Ag (I)		2 mol/L HCl			pH 5.6		
	pH 7	HNO <sub>3</sub>	Au (III)	Pd (II)	Pt (IV)	Hg (II)	Cu (II)	Zn (II)
PCOON	3.16	0.11	1.28	0.41	0.99	3.56	1.61	0.94
PCSSN	4.47	1.58	7.11	3.89	2.62	2.51	2.05	1.02

**Table VI Electron Binding Energies (ev)**

Orbits	PCS <sub>5</sub>	PCS <sub>5</sub> -Au (III)	Δ	PCS <sub>5</sub> -Pd (II)	Δ	PCS <sub>5</sub> -Pt (IV)	Δ
O <sub>1s</sub>	532.3	532.6	0.3	532.5	0.2	532.3	0
N <sub>1s</sub>	399.5	400.0	0.5	400.2	0.7	399.8	0.3
S <sub>2p</sub>	163.3	164.3	1.0	164.6	1.3	163.8	0.5

Δ. difference

Table VI shows that when PCS<sub>5</sub> chelated Au(III), the EBE of orbits O<sub>1s</sub>, N<sub>1s</sub>, and S<sub>2s</sub> in metal chelate PCS<sub>5</sub>-Au(III) are higher than those of the pure resin PCS<sub>5</sub>. The differences between chelating resin and metal chelates are 1.0 (S<sub>2p</sub>) > 0.5 (N<sub>1s</sub>) > 0.3 (O<sub>1s</sub>). Following the photoelectron spectroscopy theory, these results imply that electron densities of these atoms are reduced after chelating adsorption. Similar phenomena and regularities occur in metal chelates PCS<sub>5</sub>-Pd(II) and PCS<sub>5</sub>-Pt(IV). Thus it may be inferred that during the chelating adsorption the metal ions are electron acceptors and the atoms S, N, and O are electron donors. We also infer that of the S, N, and O atoms, S is the strongest electron donor. Thus the adsorbing capacities of PCS resins for the metal ions increases with higher S content.

The investigation of the EBEs of some orbits in metals, metal ions, and metal chelates are shown in Table VII.

Au(III), Pd(II), Pt(IV) exist in forms of HAuCl<sub>4</sub>, HPdCl<sub>3</sub>, and H<sub>2</sub>PtCl<sub>4</sub> in the medium of 2

mol/L HCl. It was found that the EBEs of these ions decreased after the chelating adsorption, further proof that metal ions accept electrons from atoms S or N or O during chelating. Finally we may infer that the basis of the chelating adsorption is a chemical adsorption. The stability of the chelates can be explained by the theory of hard and soft acids and bases. Au(III), Pd(II), and Pt(IV) are soft or medium acids and S, N, and O are soft or medium bases.

## CONCLUSION

The chelating resins containing mercapto and amino groups were simply synthesized from chitosan. These resins have remarkable adsorbing capacities and rates for some noble metal ions. Thus they can be used to concentrate and retrieve precious metal ions from dilute solutions. XPS studies show that the chelating adsorption is a chemical adsorption.

**Table VII Electron Binding Energies of Metals (ev)**

Orbit	HAuCl <sub>4</sub>	PCS-Au (III)	Au	HPdCl <sub>3</sub>	PCS-Pd (II)	Pd	H <sub>2</sub> PtCl <sub>4</sub>	PCS-Pt (IV)	Pt
4f <sub>5/2</sub>	90.4	89.1	87.5				76.7	76.5	74.2
4f <sub>7/2</sub>	87.0	85.4	83.8				74.1	73.2	71.0
3d <sub>3/2</sub>				345.2	343.4	340.2			
3d <sub>5/2</sub>				339.8	338.1	335.1			

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