Extraction of Metal Ions from Water with Tetrapyrazolic Macrocycles Bound to Merrifield Resin and Silica Gel

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ABSTRACT: Two macrocyclic tetrapyrazolic compounds having internal cavities of different sizes of were covalently bound both to a porous silica gel and to a Merrifield resin. The ability of these sorbents to extract heavy and akali metal ion from water by a solid–liquid extraction process was studied and compared to results of classical liquid–liquid extraction with the unbound pyrazole compounds. The grafting at the surface of silica does not affect the complexing properties of the ligands. However, the hydrophobic nature of the Merrifield resin has a marked effect, especially on the selectivity of extraction between the alkali metals. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2495–2499, 2000

Key words: sorbents; metal ions; macrocyclic pyrazoles

INTRODUCTION

In recent works, a series of acyclic pyrazole compounds containing one, two, three, or four pyrazole rings were prepared and covalently bonded at the surface of a polystyrene based crosslinked resin[1] or silica gel.[2] The complexing properties of these new sorbents toward heavy metals as mercury, cadmium, lead, or alkali metals were studied. The extraction of heavy metals ions from water was good but poor results were obtained with alkali metals. More recently, the synthesis of two macrocyclic tetrapyrazolic compounds was reported.[3] Such structures are expected to form stable complexes both with transition and alkali metals.[4–11] In fact, liquid–liquid extraction experiments carried out with the compounds represented in Figure 1 were successful with both series of metal ions.[3] Thus, it was interesting to immobilize these compounds on insoluble supports. This paper reports the synthesis of these new sorbents for solid–liquid extraction, prepared by covalent bonding of the two macrocycles depicted in Figure 1 at the surface of a Merrifield resin and a silica gel. Results for metal extraction from water are also given.

EXPERIMENTAL

Starting Materials

All solvents and other chemicals were obtained from the usual commercial sources, were of analytical grade, and used without further purification.

Spherical porous silica (Silicagel Si 60, 0.063–0.200 mm) was obtained from E. Merck. It was
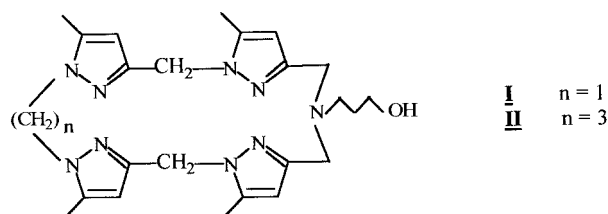
Figure 1 Representation of the macrocyclic tetra-pyrazolic ligands.

extensively washed with water and dried at 160°C for 24 h before use. Its specific area was 293 m^2/g as determined by the Brunauer–Emmett–Teller method (sorption/desorption of nitrogen). 3-Glycidoxypropyltrimethoxysilane was obtained from Janssen Chimica.

The chloride content (3.73%) in the starting Merrifield resin was determined by elemental analysis, corresponding to an exchange capacity of 1.05 mmol · g^{-1}. The pyrazole compounds (Fig. 1) were prepared as described earlier.[3]

Alcoolate Derivatives of the Hydroxy-Substituted Pyrazoles

Different routes were tried for the preparation of the alcoolate derivatives used for binding to silica or Merrifield resin: (1) sodium hydride in dimethylformamid,[12] (2) potassium hydroxide in water using tetrabutylammonium hydrogenosulfat as catalyst,[13] and (3) potassium carbonate in dimethylformamide (Williamson reaction)[14] giving poor yields. For compound *I*, a convenient method was that of Hakomori often used for the permethylation of carbohydrates. It consists in the preliminary formation of a sodium salt of dimethylsulfoxide[15] to which compound **I** is added (Fig. 2).

Compound **II** was converted into the alcoolate salt derivative using equimolar amounts of sodium metal in tetrahydrofuran.

Synthesis of Epoxy-Substituted Silica (Fig. 3)

Various procedures were described in the literature for the coupling of an epoxysilane to silica[16–18] and a modification of one of these was used in this work[17]: to porous silica (10 g), dried at 200°C for 24 h, and then stirred in 300 mL of toluene previously dried over metal sodium, were added 240 μL of triethylamine (potassium hydroxide dried) and 13.3 mL of 3-glycidoxypropyltrimethoxysilane. The mixture was stirred and refluxed under nitrogen overnight. Then the substituted silica was filtered off and washed on a
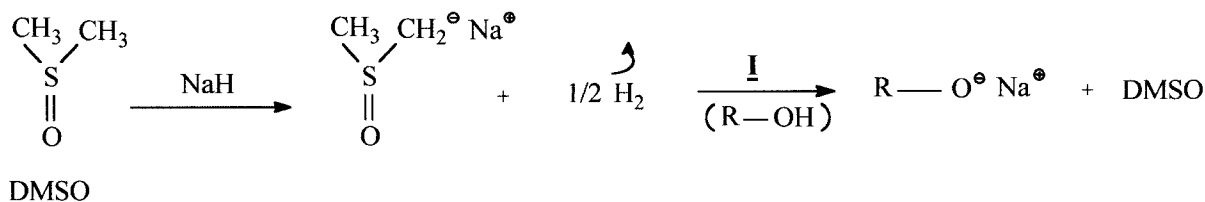

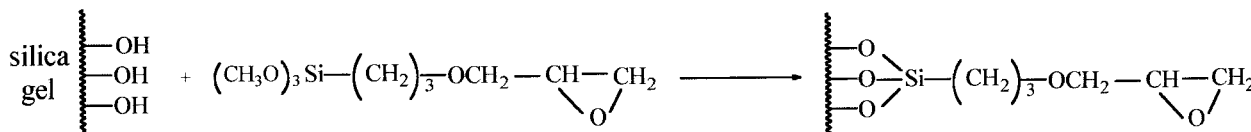**Figure 2** Preparation of the alcoolate of ligand I.

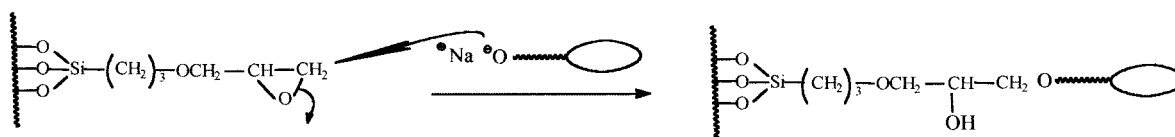**Figure 3** Synthesis of the epoxy silica.

Figure 4 Coupling of the alcoolates to the epoxy resin.

Figure 5 Coupling of the alcoolates to the Merrifield resin.

glass filter-funnel with toluene, acetone, and diethyl ether (150 mL of each) and finally dried.

Synthesis of Pyrazole-Silica Gel Bound (Fig. 4)

The amount of 0.8 mmol of the pyrazole alcoolate was added to a suspension of epoxy-substituted silica (1 g) in 30 mL of dimethylformamide. The mixture was stirred and refluxed under nitrogen for 24 h. The solid material was filtered; the residue was washed with DMF, methanol, chloroform, ethyl ether, and deionized water, and finally dried.

Binding to Merrifield Resin (Fig. 5)

The alcoolates were bound to the Merrifield resin by a SN_2 nucleophilic substitution.

Batch Experiments

The complexation of pyrazole resins was carried out with Hg(II), Cd(II), Pb(II), Ca(II), Cs(I), K(I), Na(I), and Li(I) ions by batch equilibration method. Pyrazole resins (0.1 g) were shaken with different metal solutions (5 mL) containing $6.48 \cdot 10^{-3}M$ of metal ions. Each solution was stirred for 24 h at 25°C. The final solution was filtered and the residual concentration of metal ions was determined by atomic absorption spectrometry. Commercially available reagent-grade chemicals and distilled, deionized water were used in all experiments.

Procedure for the Liquid–Liquid Extraction Method

Fifty milliliters of a $7 \cdot 10^{-5}$ mol/L metal salt solution was added to 50 mL of a methylene chloride solution of a given pyrazole compound ($7 \cdot 10^{-5}$ mol/L). The mixture was gently shaken and the equilibrium was reached after 2 h. The residual metal concentration in the aqueous phase was determined as above.

Table I   Characterization of the Pyrazole-Bound Silica

	C %	H %	N %	μmole of ligand/g Elemental Analysis	μmole of ligand/g Thiosulfate Titration
S_I	9.361	1.136	1.214	96	100
S_{II}	9.224	1.086	1.146	91	100

Table II   Characterization of the Pyrazole-Bound Merrifield Resins

	μmole of Ligand/g	Weight of Ligand in mg/g
M_I	39	18.1
M_{II}	240	118.7

Spectroscopic Measurements

At the different steps of the synthesis, the samples were characterized by IR and solid state NMR spectroscopy (CP MAS CXP 300 MHz).

RESULTS AND DISCUSSION

Characterization of the Sorbents

The amount of epoxy spacer groups grafted on silica was determined both by elemental analysis of carbon and by titration with sodium thiosulfate as described in literature.[19] The two methods gave concordant results at 780 $\pm$ 10 μmole of epoxy groups per gram of silica. In IR spectroscopy, the strong decrease of the large ν_{OH} adsorption around 3300 cm^{-1} and the appearance of a ν_{C-H} sharp band at 3030 cm^{-1} attested the grafting of the epoxy groups on the silica surface. The ^{13}C solid-state NMR spectrum recorded after hydrolysis of the epoxy groups to diols with diluted sulfuric acid (pH 2, 90°C, 1 h) also revealed the presence of the spacer arm.

The amount of pyrazole ligand bound to silica was determined both by elemental analysis of nitrogen and titration of the residual epoxy groups giving results in good agreement (Table I). The amount of bound pyrazole ligand is rather low compared to the available epoxy groups (about 15%). The specific area of the silica is not significantly affected by the grafting reaction: 306 m^2/g for S_I and S_{II}.

IR spectrophotometry and elemental analysis were used to characterize the pyrazole-modified Merrifield resins. The IR spectrum of the native Merrifield resin exhibits a band at 1260 cm^{-1}, typical of the C—Cl bond that disappears during substitution of the resin. A strong band at about 1150 cm^{-1} assigned to the ν(C—O—C) appears in the spectra of M_I and M_{II} polymers.

From the elemental analysis of nitrogen, the amount of pyrazole grafted was obtained (Table II).

Table III   Yields of Extraction of Various Heavy and Alkali Metal Ions[a]

	Mercury (1.10 Å)	Cadmium (0.92 Å)	Lead (1.20 Å)	Calcium (0.99 Å)	Cesium (1.69 Å)	Potassium (1.33 Å)	Sodium (0.98 Å)	Lithium (0.60 Å)
Free ligand **I**	59	46	50	5	20	40	36	25
Silica S$_\mathbf{I}$	70	46	48	6	20	39	36	25
Merrifield resin M$_\mathbf{I}$	30	31	30	0	0	10	30	0
Silica S$_4$[b]	52	20	32	0	0	0	0	0
Merrifield resin M$_4$[b]	52	20	25	0	0	15	30	0
Free ligand **II**	60	40	50	6	45	39	39	29
Silica S$_\mathbf{II}$	70	37	50	5	46	41	38	28
Merrifield resin M$_\mathbf{II}$	20	17	10	6	0	8	18	0

[a] Yield of complexation calculated as μmol of metal/μmol of pyrazole.
[b] Silica and Merrifield resin bearing the acyclic pyrazole analogue of **I** and **II** (Refs. 1 and 2).

Complexation with Metal Ions

The results are given in Table III and expressed as yield of complexation calculated as μmole of metal per μmole of tetrapyrazolic compound. It was first checked that none of the unfunctionalized sorbent (native silica, epoxy silica, and Merrifield resin) was able to complex the different metal ions.

The affinity of the free ligands **I** and **II** toward heavy metal ions is high. It is not significantly affected when going to silica-supported ligands, but the yield of extraction decreases when considering Merrifield resin-supported ligands. This is probably a consequence of the rather hydrophobic nature of the surface. In addition, the spacer arm is short compared to that used for coupling to silica. The comparison with the acyclic analogs of **I** and **II** shows that the cyclic compounds are more efficient at least when free or bonded to silica. The reverse seems to apply for the Merrifield resins at least for mercury.

The cyclic tetrapyrazolic compounds either free or bonded are efficient towards alkali metal ions. Ligand **I** has a high affinity for potassium and sodium whereas compound **II** is more efficient for cesium. This is undoubtedly related to the size of the cavity and to the ionic radii. The yields and selectivity are entirely maintained when going to silica supports. On the contrary, Merrifield resins are able to extract only sodium and in a less extent potassium. Such a result was also obtained with acyclic ligands and is probably related to specific interactions with the resin surface. As a conclusion, it is clear that the complexing properties of the macrocyclic tetrapyrazolic compounds are kept when bonded to silica surface, with respect to yield and selectivity. This indicates that the complexation reaction occurs in aqueous solution with no restriction due to steric hindrance for example. The choice of a long spacer arm seems to be convenient. The results with the Merrifield-bonded ligands are quite different. The vicinity of the hydrophobic surface changes the yields and the selectivity. Extraction of potassium and sodium from a mixture containing other alkali metals seems possible. These sorbents are also able to remove heavy metal ions from water. Future work will involve the grafting of these promising ligands to more hydrophilic organic resins.

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