

The importance of hydrogen bonding in the complexation of lanthanide ions by polymer-bound malonamide-type ligands

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ABSTRACT

Polymer-bound malonate ligands modified with diethylenetriamine (DETA-MAm) are prepared and the lanthanide ion affinities from solutions of 0.001–8 M HCl are quantified. A mechanism is proposed. The affinities are not due to the triamine ligand alone or the adjacent carbonyl sites alone: protonation of the carbonyl oxygen triggers formation of an iminium ion and it acts as an ion-exchange site. Two competing reactions occur during binding: electrostatic attraction of $[\text{Ln}(\text{H}_2\text{O})_x\text{Cl}_4]^-$ by the protonated ligand and (partial) loss of the waters of hydration. The affinity and selectivity are affected by substituents on the iminium ($\text{C}=\text{NRR}'(+)$) ion. Research with tetramethylmalonamide showed that its two methyl groups at the iminium site weaken the positive charge and decrease its affinity for the chlorocomplexes of the later lanthanides; DETA-MAm has at its amide nitrogen only one $-\text{CH}_2-$ (and one H) moiety and therefore is a stronger but less selective ligand since electrostatic attraction is more dominant in the overall mechanism. The higher affinities of malonate monoamidated with ethylenediamine (EDA-MAm) and decreased affinities for those amidated with ethanolamine (EA-MAm) suggest that the protonated $-\text{NH}-$ stabilizes the lanthanide chlorocomplex.

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1. Introduction

Ionic recognition [1] is important to developing ion-selective electrodes [2], sensors [3], and materials for separations science [4]. In order to attain high selectivities toward targeted ions, understanding the mechanism of ionic recognition is of continuing interest. Recognition by a ligand for a metal ion within a given set of ions has been defined as needing two opposing mechanisms with a changeover from one dominant mechanism to another as the series progresses [5].

The lanthanides form an important series of metal ions, with applications as diverse as luminescent probes in medicine [6] and as catalysts [7]. Moreover, their isolation from nuclear wastes would be advantageous [8]. They have a well-defined set of properties (ionic radius, charge density, hydration enthalpy, etc.), similar polarizabilities, and complexes with similar geometries and minimal covalent interactions [9]. Immobilized *N,N,N',N'*-tetramethylmalonamide (TMMA) preferentially binds Tb, Dy, and Eu from highly acidic solutions [10]. The proposed mechanism entails initial protonation of one of the carbonyl oxygens, then hydrogen bonding between the proton and a neighboring carbonyl oxygen triggers formation of the iminium site which acts as the site of ion-exchange (Scheme 1). Ionic recognition is achieved through a

mechanism in which two opposing reactions—electrostatic attraction of $[\text{Ln}(\text{H}_2\text{O})_x\text{Cl}_4]^-$ or $[\text{Ln}(\text{H}_2\text{O})_x(\text{NO}_3)_4]^-$ by the protonated ligand and (partial) loss of the waters of hydration—dominate at different points along the lanthanide series. In this report, we probe the general nature of the mechanism with three new amide ligands: malonate is amidated with diethylenetriamine (DETA), ethylenediamine (EDA) and ethanolamine (EA).

2. Experimental

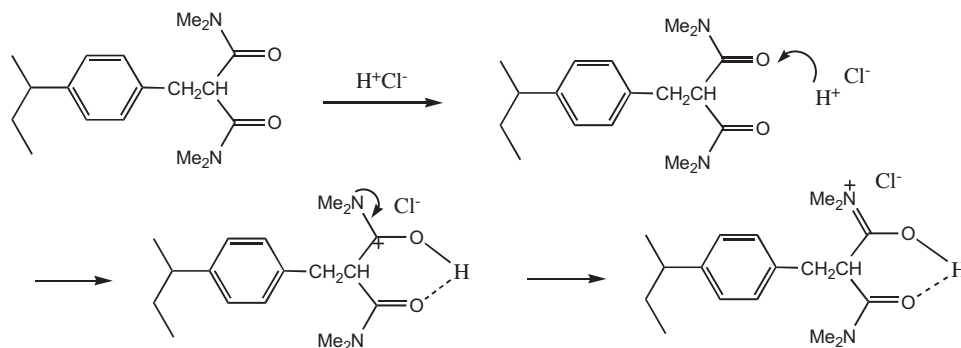
All chemicals were obtained from Sigma–Aldrich or Acros and used without further purification unless otherwise noted. The preparation of the crosslinked poly(vinylbenzyl chloride) [poly-VBC] beads has been described [11]. A particle size of 0.25–0.42 mm was used. Reactions at other than room temperature or reflux were regulated with a temperature controller. Water for metal ion studies and analytical determinations was filtered through a Millipore Direct Q-5 system and had a resistivity of 18.2 MΩ-cm.

2.1. Synthesis of polyVBC-bound diethyl malonate

Diethylmalonate (9.1 mL, 60 mmol) was dissolved in 100 mL 1-methyl-2-pyrrolidone (NMP) and 2.3 g NaH (60% dispersion, 57 mmol) was added in portions. The mixture was heated at 60 °C for 2 h, 2.0 g of polyVBC beads swollen in 50 mL of NMP were added, and the reaction stirred at 80 °C for 17 h. The beads were

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Scheme 1. Tetramethylmalonamide activation through iminium ion formation.

recovered and washed with NMP and water. The resin was hydrolyzed in order to determine the degree of functionalization: 1.8 g of KOH in 12 mL H₂O and 10 mL of ethanol were added to 1.5 g of the beads swollen in 60 mL of 1,4-dioxane, then refluxed for 36 h. The beads were washed with water, placed in a glass frit funnel, and conditioned with 1 L each of H₂O, 1 M NaOH, H₂O, 1 M HCl, and H₂O.

2.2. Synthesis of diethylenetriamine (DETA) resin

PolyVBC (5.0 g) was contacted with 100 mL NMP for 2 h and then 50 mL DETA was added. The mixture was stirred at 80 °C for 17 h. The beads were recovered and washed with NMP, water and MeOH, placed in a glass frit funnel, and conditioned as above.

2.3. Amidation of malonate with DETA, ethylenediamine (EDA) and ethanolamine (EA)

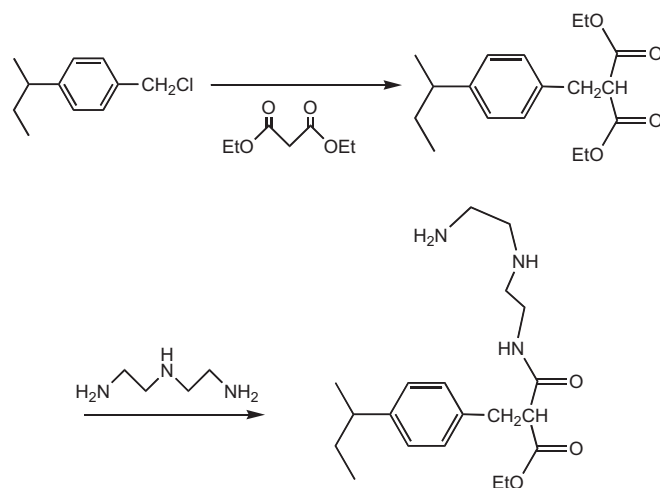
Malonate resin (2.0 g) was contacted with 50 mL of DETA, EDA or EA for 2 h. The mixture was stirred at 110 °C for 17 h. The beads were recovered and washed with NMP, water and MeOH, placed in a glass frit funnel, and conditioned as above.

2.4. Amidation of monocarboxylic acid resin with DETA

The preparation of the monocarboxylic acid resin has been described [6]. Dry carboxylic acid resin (2.0 g) was refluxed in 100 mL SOCl₂ for 48 h. After excess SOCl₂ was removed, the resulting resin was washed with toluene twice and 1,4-dioxane once. 1,4-Dioxane and DETA (50 mL each) were then added and the mixture stirred at 110 °C for 17 h. The beads were recovered, washed with 1,4-dioxane and water, placed in a glass frit funnel, and conditioned as above.

3. Results

Diethyl malonate was immobilized onto polyVBC and amidated with DETA (Scheme 2). The chlorine capacity of the malonate resin is 1.24 mmol/g and its acid capacity after hydrolysis is 6.17 mmol/g, which calculates to 80% functionalization. Resins produced from reaction of the malonate with DETA have an average nitrogen capacity of 6.81 (±0.10) mequiv/g. Allowing for 80% functionalization to the malonate, the theoretical nitrogen capacity for monoamidation of the diester is 7.42 mequiv/g. The FTIR spectrum of the DETA-malonate amide shows a band at 1671 cm⁻¹ due to the amide carbonyl and a band at 1725 cm⁻¹ associated with the ester carbonyl. The malonate diester has a band at 1732 cm⁻¹ due to the ester C=O stretch. The red shift of the C=O band from 1732 to 1725 cm⁻¹ is due to the functional group on the neighboring car-



Scheme 2. Immobilization of diethyl malonate and amidation with DETA (DETA-MAm).

bonyl. Similar shifts were observed for the EDA-malonate amide (1726 cm⁻¹) and EA-malonate amide (1727 cm⁻¹). These results are consistent with the uniform formation of DETA-malonate monoamide (DETA-MAm), EDA malonate monoamide (EDA-MAm), and EA malonate monoamide (EA-MAm).

In order to probe the importance of adjacent carbonyl groups to the complexation of the lanthanides, a monocarboxylic acid resin was amidated with DETA via the acyl chloride (Scheme 3). The nitrogen capacity of 6.45 mequiv/g (2.15 mmol/g ligand capacity) corresponds to 57% yield (calculated ligand capacity at 100% functionalization is 3.75 mmol/g). The most likely side reaction is that of a terminal amino group in an amide with a neighboring acyl chloride. The FTIR spectrum of the amidated acid (DETA-AmA) shows a strong band at 1647 cm⁻¹, confirming the amide group. No peaks were evident at 1732 or 1701 cm⁻¹, indicating the absence of diester and acid groups, respectively. The DETA resin was prepared in order to determine whether the observed metal affinities by the DETA-MAm resin were affected by the triamine ligand alone. That reaction goes to completion, as indicated by the absence of chloride and a nitrogen capacity of 8.72 mequiv/g (some bridging of two benzyl moieties by a single DETA is indicated since the theoretical capacity for complete functionalization is 11.9 mequiv/g).

3.1. Effect of HCl concentration on the lanthanide affinities of the DETA-MAm resin

The lanthanide affinities of the DETA-MAm resin from HCl solutions were quantified (Fig. 1). The distribution coefficients increase

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