

Chelating Behavior between Metal Ions and EDTA in Sol–Gel Matrix

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Ethylenediamine tetraacetic acid (EDTA) was encapsulated in a sol–gel-derived optically transparent glass. The complexation of metal cations, Cu(II), Ni(II), Fe(III), Cr(III), Co(II), Mn(II), Pd(II), and Ir(IV), with EDTA in solutions and in gels was evidenced by the formation of individual colors. A comparison of the absorption spectra of M^{n+} /EDTA in solution, M^{n+} /EDTA in gel, and M^{n+} /EDTA complex in gel was performed. The results show that (i) all six chelating sites in EDTA remain active in a sol–gel matrix as they bind readily with Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} , (ii) EDTA is rigidly oriented in a sol–gel matrix that inhibits its heat- or catalyst-assisted complexation with Cr^{3+} , Co^{2+} , and Mn^{2+} , (iii) no absorption spectral shift for the d–d metal transitions was observed compared to those in solution, yet a 10–30 nm shift for the MLCT transitions of Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , Ir^{4+} was detected, and (iv) the level of sensitivity in detecting metal cations using EDTA in gel is at least an order of magnitude higher than that in solution. The response time of M^{n+} /EDTA complexation in gel is quite short, ranging from 1/30 to 15 min. This response time and the mode of sensing device guarantee that no leaching of EDTA from the sol–gel matrix is possible.

Introduction

Room temperature polymerization of metal alkoxides enables the encapsulation of thermally unstable compounds, such as organic, metallorganic, and biological species, in inorganic porous glasses. The glass matrix serves as a solid support for reactive materials in which the dopant molecules are capable of responding chemically to the environment through the pore space.¹ The sol–gel doping method is gaining popularity as a result of its generality and simplicity. The concept of the sol–gel method is intermediate between impregnation and covalent bonding techniques and has provided a general and inexpensive route for the immobilization of reagents. A variety of photo-metric reagents for the detection of anions, cations, redox species, and airborne pollutants have been successfully immobilized in silica, titania, and other xerogels.² The silicate matrix in sol–gel materials is usually formed by hydrolysis of an alkoxide precursor, followed by condensation, to yield a polymeric oxo-bridged SiO_2 network.³

The highly porous and optically transparent silicate gel matrix has been used in both chemical and biochemical sensors.^{4–7} Zusman et al.⁸ have demonstrated the success of doped gels in chemical analysis. They encapsulated a series of chemical agents that are sensitive to selected analytes in monolithic xerogel glass blocks. By monitoring the characteristics of color changes in the doped gels, they illustrated that metal cations such as Fe^{3+} , Al^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Pb^{2+} , as well as changes in pH, could be detected. The detection of hexavalent chromium by malachite green doped sol–gels has been illustrated⁹ where Cr(VI) concentrations on the order of 5 ppb are detectable. The incorporation of porphyrin in a sol–gel-derived matrix has been employed to detect Hg^{2+} , but other metal cations such as Zn^{2+} , Cd^{2+} , and Pd^{2+} were shown to interfere with detection.¹⁰

Ethylenediamine tetraacetic acid (EDTA) is a well-known chelating agent¹¹ with six potential sites (i.e., a hexadentate ligand) available for binding with metal cations composed of four carboxyl and two amino groups. When EDTA is dissolved

in water, the ligand behaves like an amino acid with double zwitterions. EDTA chelates with metal ions in a 1:1 ratio regardless of the charge of the cation. EDTA forms a chelating complex with all cations, and most of these complexes are sufficiently stable. This stability results from the multiple sites within the ligand that give rise to a cage-like structure in which the cation is effectively surrounded and isolated from solvent molecules. Evidently, EDTA forms colored complexes with Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} in buffer solutions (referred to as class I) and with Cr^{3+} and Co^{2+} at boiling temperature, as well as with Mn^{2+} in the presence of acetic acid and sodium bismuthate (referred to as class II).¹²

The encapsulation of EDTA in the sol–gel-derived optically transparent glass has been reported recently.¹³ The report focused mainly on leaching behavior as a function of the timing of the addition of EDTA in silica gels. In this paper, we investigate the chelating behavior between metal cations and EDTA ligand in the silica matrix. The observed new phenomena in chelation chemistry under the confined environment are geared toward analytical applications. Two classes, I and II, of metal cations are used to form colored M^{n+} /EDTA complexes in silica glass. The results are discussed in terms of the effects of sol–gel matrix on the chelating activity of six ligand sites and on the molecular rigidity of EDTA ligand. We also illustrate the capability of using EDTA encapsulated in sol–gels to detect metal cations and, more importantly, to differentiate the d–d metal transitions from that of the metal–ligand charge transfer (MLCT) transitions in the absorption spectra of M^{n+} /EDTA complexes.

Experimental Section

The disodium salt of ethylenediamine tetraacetic acid used to prepare the EDTA-doped silica gels was purchased from Fisher Scientific. A 0.1 M EDTA sample was prepared by using a 0.1 M phosphate buffer of pH 6.5. The silica sol was prepared by dispersing 3.0 mL of tetramethoxysilane (98% TMOS, Aldrich) in 11.0 mL of methanol. The gel was synthesized by mixing 2.0 mL of the sol with 2.0 mL of EDTA solution and catalyzed by adding 2 drops of 0.04 M HCl. The resulting solution was transferred into a 4.0 mL polystyrene cuvette and

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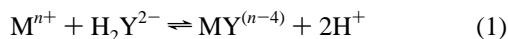
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then covered with Parafilm. The gelation time was about 3 h. The gels were allowed to develop and dry at room temperature until stabilization of the weight had been completed. Concentrations greater than 0.1 M of EDTA in the gel tend to result in precipitation and unclear gels. Moreover, using buffers of a pH higher than 6.5 to incorporate EDTA in the gel can lead to a fast gelation and produce nontransparent gels. One way to increase the pH of the sol–gel matrix and make the gels more optically transparent is to add two to three drops of $\text{NH}_3/\text{NH}_4^+$ buffer solution, pH 10, to the gels during the gelation stage.

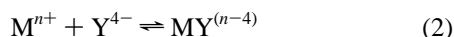
Solutions of Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , Ir^{4+} , Cr^{3+} , Co^{2+} , and Mn^{2+} were prepared by dissolving the corresponding metal chloride (or acetate) salt in deionized water. Detection of each of the class I metal cations, Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} was performed by an addition of two to three drops of the metal ion solution to the transparent colorless EDTA-doped gel. Diffusion of the metal cation through the microchannels, or pores, of the sol–gel matrix resulted in the formation of $\text{M}^{n+}/\text{EDTA}$ complex in gel and the development of a distinguishable color. The class II metal cations, Cr^{3+} , Co^{2+} , and Mn^{2+} required that the colored $\text{M}^{n+}/\text{EDTA}$ complex first be produced in the solution and then encapsulated in a silica matrix. Light absorption spectra of metal cations were recorded on a Shimadzu UV300 UV–vis spectrophotometer. The vibrational spectra of EDTA in solution and in gel were investigated by using a Bruker Vector 22 FTIR spectrophotometer.

Results and Discussion

Detection and Sensitivity of Class I Metal Cations in EDTA-Doped Gels. EDTA has a simplified formula, H_4Y , and forms 1:1 complexes under ordinary conditions with most metal cations. The frequently used EDTA compound in analytical reactions is the disodium salt, $\text{Na}_2\text{H}_2\text{Y}$ (or H_2Y^{2-}). The complexation of $\text{M}^{n+}/\text{EDTA}$ in solution follows the equation



It is shown that the ionization of the complex $\text{MY}^{(n-4)}$ is dependent upon the H^+ concentration of the solution. The stronger the complex, the lower must be the pH of the solution for total ionization of the complex to occur. The extent to which $\text{M}^{n+}/\text{EDTA}$ complex formation occurs is usually expressed by a formation constant, K , for the following association reaction:



The formation constants of $\text{M}^{n+}/\text{EDTA}$ complexes (in log K , at 20 °C and ionic strength = 0.1) were determined¹² to be 25.1 for Fe^{3+} , 18.5 ± 0.6 for Pd^{2+} , 18.4 for Cu^{2+} and Ni^{2+} , 16.1 for Co^{2+} , and 13.5 for Mn^{2+} .

The solution color of Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , Ir^{4+} , Cr^{3+} , Co^{2+} , and Mn^{2+} (i.e., the metal chloride/acetate salt in deionized water) is light blue, green, yellow, brown, gray, green, red, and colorless, respectively. Upon complexation with EDTA, the colored complexes of $\text{M}^{n+}/\text{EDTA}$ in buffer solutions become sky blue for Cu^{2+} , navy blue for Ni^{2+} , deep violet for Fe^{3+} , stable yellow for Pd^{2+} , pale yellow for Ir^{4+} , violet for Cr^{3+} , violet for Co^{2+} , and ruby red for Mn^{2+} ion. The procedure for synthesizing the $\text{M}^{n+}/\text{EDTA}$ complex is simple, but it varies for different metal ions. A direct mixing of a metal cation solution and an EDTA buffer solution would generate the colored complexes of $\text{M}^{n+}/\text{EDTA}$ for Cu^{2+} , Ni^{2+} , Pd^{2+} , and Ir^{4+} ions. With EDTA and 30% hydrogen peroxide in ammoniacal solution, iron(III) yields a deep violet complex $\text{FeY}^- \cdot \text{H}_2\text{O}_2$, which is stable at normal temperature for several hours. Heating

the solution to boiling for a few minutes is needed to develop the color of the $\text{M}^{n+}/\text{EDTA}$ complex for Cr^{3+} and Co^{2+} ions. The generation of colored $\text{Mn}^{2+}/\text{EDTA}$ complex in solution requires the presence of acetic acid and sodium bismuthate.¹²

Figure 1 shows the colorimetric detection of Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} ions by EDTA-doped silica gels. The optically transparent colorless EDTA doped sol–gel is placed in the center of Figure 1. The middle layer displays the solutions of 8.0 g/L Cu^{2+} , 5.0 g/L Ni^{2+} , 1.0 g/L Fe^{3+} , 0.15 g/L Pd^{2+} , and 0.1 g/L Ir^{4+} in cuvettes. For each metal ion, two to three drops of solution were added to the EDTA-doped silica gel. The resultant colored complexes of $\text{M}^{n+}/\text{EDTA}$ gel remain optically transparent and as in the outer layer of Figure 1. Following Beer's law, the spectrophotometric detection ranges of metal cations complexing with EDTA in solution are 30–8000, 400–50 000, 4–500, 6–95, and 5–60 ppm for Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} ion, respectively.¹² The colored complexes of $\text{M}^{n+}/\text{EDTA}$ gels shown in the outer layer of Figure 1 were produced by adding 1.6 mg Cu^{2+} , 1.0 mg Ni^{2+} , 0.2 mg Fe^{3+} , 0.03 mg Pd^{2+} , and 0.02 mg Ir^{4+} aqueous solution to the colorless EDTA-doped silica gel. All $\text{M}^{n+}/\text{EDTA}$ gels show a strong color and have an optical absorbance of 0.3–1.0, indicating that the detecting limit of metal ions by EDTA-doped silica gels should be at least an order of magnitude better than that illustrated in Figure 1. The response time for developing the desired color of $\text{M}^{n+}/\text{EDTA}$ gels is 3, 2, 2, 600, and 900 s for Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} ion, respectively. The high level of sensitivity in $\text{M}^{n+}/\text{EDTA}$ gels is achieved because the ions are allowed to diffuse into the matrix of the gel where they react with the EDTA and remain trapped.

The results in Figure 1 give the indication that all six chelating sites in EDTA remain active in the sol–gel matrix. This is in agreement with the report of Oka et al.¹³ that no direct bonding (i.e., an acetate polymerization in which the EDTA molecule forms a direct bond with the hydrolyzed alkoxide) or hydrogen bonding (i.e., a weak attractive force forms between one of the acetate groups on the EDTA molecule and a hydroxyl group on the alkoxide) was found between the EDTA molecule and the gel matrix. Weakly attracted van der Waals forces may exist between EDTA and the pore surface, or the molecule may be strictly hindered within a pore. The locations and the weak physical interactions of EDTA in silica gels tend to promote a leaching of EDTA out of the gel matrix.¹³ When the EDTA-doped silica gels were soaked or flooded with water as the solvent, the percentage of the EDTA leached out of the gel matrix and dissolved in the water solution was determined as 5%, 25%, 40%, and 50% after 5, 60, 600, and 900 s of immersion, respectively. It is important to note that the problem of EDTA leaching out of the gels should not affect the sensing design of Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} ion in the EDTA-doped silica gel. This is due to the fact that the colorimetric determination of metal cations using EDTA encapsulated in a sol–gel matrix displays a fast response time and requires only two to three drops of analyte.

Identification of the d–d and MLCT Transitions of $\text{M}^{n+}/\text{EDTA}$ Complexes. The UV–visible absorption spectra of $\text{M}^{n+}/\text{EDTA}$ in solution are quite broad and structureless. The spectral maximum is identified at around 680, 560, 460, 320, and 280 nm for Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} EDTA complexes, respectively. For $\text{Cu}^{2+}/\text{EDTA}$ in solution, the transition at 680 nm has been assigned to the d–d transition and the MLCT absorption typically begins at about 500 nm.¹⁴ The spectral band at 560 nm for $\text{Ni}^{2+}/\text{EDTA}$ in solution is due mainly to the charge-transfer absorption of $xz-xy$ type and a small mixing with the d–d character of $(x^2 - y^2)-xy$ type.¹⁵

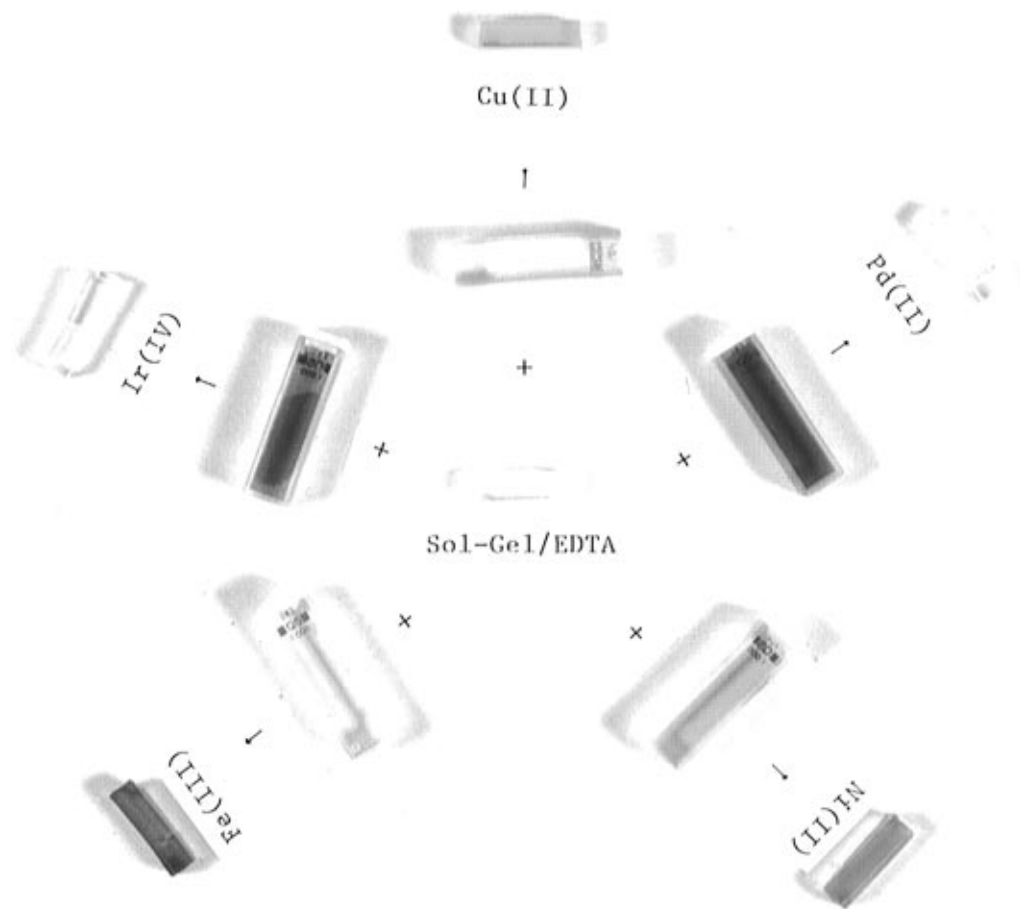


Figure 1. Colorimetric detection of metal cations by EDTA-doped silica gels: (center) EDTA-doped xerogel; (middle layer) aqueous solutions of metal cations; (outer layer) M^{n+} /EDTA-encapsulated silica gels.

The strong oxidizing power of Fe(III) gives the single most well-known iron(III) charge-transfer (CT) band in association with the intense red color.¹⁴ For the Fe^{3+} /EDTA complex in solution, the absorption band at 460 nm is one of the few fairly strong CT transitions that often obscure the very low-intensity d–d band. The available spectroscopic data¹⁴ indicate that the absorption band at 320 nm for Pd^{2+} /EDTA in solution is best assigned to a charge-transfer transition mixed with some weak d–d character, whereas that at 280 nm for Ir^{4+} /EDTA in solution belongs to a d–d transition split by spin–orbit coupling.

The absorption spectra recorded for silica gels of M^{n+} /EDTA complexes (displayed in the outer layer of Figure 1) had a spectral maximum at 680, 540, 475, 280, and 280 nm for $M^{n+} = Cu^{2+}$, Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+} , respectively. No spectral shift was observed for the spectra of Cu^{2+} /EDTA and Ir^{4+} /EDTA in gels as compared to those in solutions. A 15–40 nm spectral shift was recorded for the spectra of Ni^{2+} /EDTA, Fe^{3+} /EDTA, and Pd^{2+} /EDTA in gels as compared to those in solutions. Figure 2 displays the representative UV–visible spectra of (a) Cu^{2+} /EDTA in solution, (b) Cu^{2+} /EDTA in gel, (c) Ni^{2+} /EDTA in solution, and (d) Ni^{2+} /EDTA in gel. The encapsulation of EDTA in sol–gel matrix showed no major effect on the d–d transitions of Cu^{2+} /EDTA and Ir^{4+} /EDTA complexes. However, the metal–ligand or ligand–metal charge-transfer transitions were quite sensitive to the chelating strength between the metal (i.e., Ni^{2+} , Fe^{3+} , or Pd^{2+}) and EDTA. The change in the chelating strength of M^{n+} /EDTA in gel compared to that in solution is presumably due to the fact that the EDTA molecule is rigidly and restrictedly oriented in the pores of the silica matrix.

Chemical Nature of EDTA Encapsulated in Sol–Gel Matrix. As illustrated in Figure 1, the colored M^{n+} /EDTA

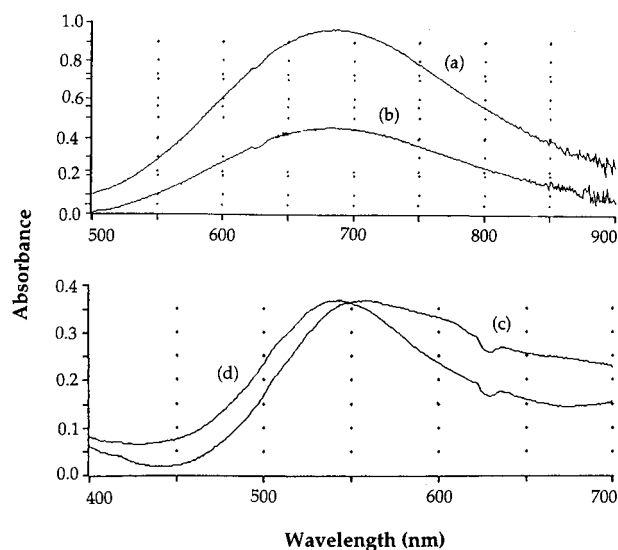


Figure 2. UV–visible spectra: (a) Cu^{2+} /EDTA in solution; (b) Cu^{2+} /EDTA in gel; (c) Ni^{2+} /EDTA in solution; (d) Ni^{2+} /EDTA in gel.

complexes in gels were easily synthesized by adding two to three drops of an aqueous solution of class I metal cations (e.g., Cu^{2+} , Ni^{2+} , Fe^{3+} , Pd^{2+} , and Ir^{4+}) to the colorless EDTA-trapped silica gel. The same procedures do not work for the class II metal cations, i.e., Cr^{3+} , Co^{2+} , and Mn^{2+} . The colored M^{n+} /EDTA complexes in gels for the class II metal cations can be produced only by forming the M^{n+} /EDTA in solutions first, followed by trapping the colored complexes in a gel matrix. The differences between the class I and class II metal cations are the following.¹² (1) The formation of colored M^{n+} /EDTA

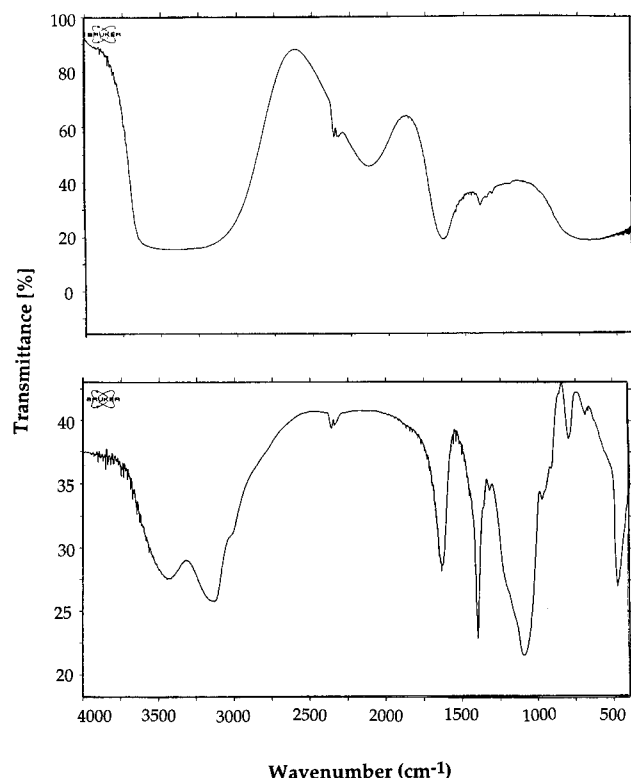


Figure 3. FTIR spectra of EDTA: (top) in aqueous solution; (bottom) in silica gel matrix.

complexes for Cr^{3+} and Co^{2+} ions is a thermal-activated process that requires boiling the solution for a few minutes. (2) The generation of a colored $\text{Mn}^{2+}/\text{EDTA}$ complex in solution requires the presence of acetic acid and sodium bismuthate. Even though the six chelating sites in EDTA remain active when the molecule is entrapped in the silica gel, the encapsulated EDTA molecules should be more rigid and should have a restricted molecular motion resulting from the shape, size, and rigidity of the sol-gel cage.⁴⁻⁷ The molecular rigidity of the entrapped EDTA in pore space could prohibit the thermal-activated and catalyst-assisted processes from occurring.

EDTA is a well-known chelating agent for heavy metal ions because, when EDTA is dissolved in water, the ligand behaves like an amino acid with double zwitterions. Figure 3 shows the FTIR spectra of EDTA in aqueous solution (top) and in a silica gel matrix (bottom). The infrared spectra of EDTA have been reported.¹⁵ In solution (top spectrum of Figure 3), the spectral band at 2129 cm^{-1} is associated with the $\text{N}-\text{H}_3^+$ stretching vibration of the amino acid zwitterions, $\text{H}_3\text{N}^+|||||\text{COO}^-$.¹⁶ The spectral transitions at 1637 and 1400 cm^{-1} are, respectively, related to the antisymmetric and symmetric $\text{C}=\text{O}$ stretching vibrations of the carboxylate anion. In the sol-gel matrix (bottom spectrum of Figure 3), on the other hand, EDTA shows no vibrational band at around 2100 cm^{-1} , suggesting that EDTA in a silica gel matrix does not form a double betaine structure. However, the carboxylate ion groups

are still active in the entrapped EDTA in silica gel as evidenced by the observed spectral bands at 1637 and 1401 cm^{-1} in Figure 3 (bottom). Other spectral bands displayed in the bottom spectrum of Figure 3 are due to the vibrational modes of silica gel. The loss of a double zwitterion configuration as well as the structural flexibility of EDTA in gel may be responsible for the insensitivity to the detection of class II metal cations.

Summary

A colorimetric chemical sensor of EDTA-doped silica gel has been fabricated for detecting heavy metal ions. The level of metal cation detection and the response time required for forming colored $\text{M}^{n+}/\text{EDTA}$ complexes are at least an order of magnitude better than those in solution. For the first time, the technique of encapsulation of EDTA in optically transparent glass has been demonstrated to aid the spectral assignment between a d-d transition and a MLCT (or LMCT) transition in $\text{M}^{n+}/\text{EDTA}$ complexes. All six chelating sites in EDTA remain active in a sol-gel matrix. However, it was shown that EDTA is rigidly oriented in the pore space and that a double zwitterion structure of EDTA is not formed in silica gels.

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