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# Comparison of structural effects on Eu(III) complexes with cyclohexyl and benzene polycarboxylic acids

Gregory R. Choppin* and Mikhail Y. Redko[1]

*Department of Chemistry, Florida State University, 501 MBB 4380, Tallahassee, FL 32306-4390 USA*

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## Abstract

The thermodynamics ($\beta$, $\Delta H$, $\Delta S$) of complexation, the residual hydration of the complexed metal ion and the metal-ligand coordination number of the complexes formed by interaction of Eu(III) with 1, 3, 5-cyclohexyltricarboxylic acid, 1, 2, 3- and 1, 2, 4-benzenetricarboxylic acids, cyclohexylhexacarboxylic (CHHS) acid and benzenehexacarboxylic (mellitic) acid have been studied. The 1, 3, 5-cyclohexyltricarboxylate ligand binds by only a single carboxylate while the 1, 2, 3-, and 1, 2, 4-benzene tricarboxylate ligands bind via two carboxylates. The mellitate complexes were found to have bidentate chelation and a residual hydration number, $N_{H_2O}$, complexed Eu(III) of ca. 7 in acid-to-neutral solutions. By contrast, in the Eu-CHHS complexation, the coordination number for the ligand binding, $CN_L$, was 2 in acidic to neutral in basic solutions while the residual hydration number of the Eu(III) changed from 6 to 7 in acidic solutions to 2.5 in alkaline solutions. This is interpreted to indicate the formation of $[Eu(CHHS)(OH)(H_2O)_2]^{4-}$. The data are discussed in terms of ligand steric effects upon complexation.

## 1. Introduction

The lanthanides and actinides have strongly ionic bonds in complexes. As a consequence, the strength of such bonds is a direct function of the effective charges of the cation and of the binding site(s) of the ligand. The strength of the metal–donor atom interaction is also a function of the metal–donor distances which are strongly affected in many of the complexes by steric factors related to the structural characteristics of the ligand [1]. This is particularly true for some of the ligands used in the more advanced and more effective separations systems such as crown ethers, calixarenes, and aminopolycarboxlic acids. A better quantitative understanding of these steric factors in the complexation of the *f*-element cations would allow better modeling to design even more effective separation systems.

This study has focused on the difference in binding interactions for ligands which are built upon a cyclohexyl ring versus those that are built on a phenyl ring. Since the properties of *f*-element metal ion complexes are determined principally by ionic and steric effects, comparison of the complexation of benzonehexacarboxylic (mellitic) acid with cyclohexylhexacarboxylic (CHHS) acid can provide insight into whether the polarization within the aromatic ring of the mellitic acid enhances the complexation of the mellitate ions and, also, how the steric differences between the rigid phenyl ring of the mellitate ion, and the flexible aliphatic ring of CHHS affects the complexation properties.

The binding of Eu(III) to cyclohexylhexacarboxylic acid has been studied by potentiometry and solvent extraction to obtain stability constants which can be compared to the constants for binding to mellitic acid. These systems also have been studied by laser flourescence spectroscopy in order to obtain information on the ligand coordination number in the complex and on the residual hydration number of the complex. The stability constants of the mellitic acid systems were measured earlier [2] and the luminescence studies done in this work. In addition, some study has been done on the complexation with Eu(III) with 1, 3, 5-cyclohexyltricarboxylic and on the 1, 2, 4- , 1, 2, 3- and 1, 2, 4, 5-benzenepolycarboxylic acids.

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*Corresponding author. Fax: +1-850-644-8281.

*E-mail address:* choppin@chemifsu.edu (G.R. Choppin).

[1] Also at Department of Chemistry, Michigan State University, B-283, East Lansing, MI 48824-1322, USA.

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## 2. Experimental

### 2.1. Reagents and solutions

$NaClO_4$ (99%), $N(CH_3)_4OH \cdot 5H_2O$ (98%), $N(CH_3)_4Cl$ (97%), $Eu_2O_3$ (99.99%), the polycarboxylic benzene and hexyl acids (99%) and mellitic acid, $H_6Mel$ (99%), were purchased from Aldrich while $HClO_4$, and HCl and NaOH, both solid and standard solutions were obtained from Fischer. $H_6CHHS \cdot H_2O$ (>99%) was a gift from "Societe Suisse Des Explosifs".

Aqueous stock solutions of $Eu(ClO_4)_3$ (0.043 M) were prepared by dissolving 0.780 g $Eu_2O_3$ (99.99%), Aldrich) in an excess of fuming 60% $HClO_4$ (Fischer), dissolving the precipitate in doubly deionized $H_2O$ and diluting to 100 mL. The concentration was determined by complexometric titration with EDTA in the presence of xylenol orange indicator [3]. Stock solutions of the ligands were prepared by dissolving 0.5 mm of a ligand in 0.1 M $NaClO_4$. For the laser experiments, a millimole of $Eu(ClO_4)_3$ was added to the ligand solution and the solution (or suspension) diluted with doubly distilled water to produce solutions of 0.005 M Eu(III), 0.005 M ligand and 0.10, 1.00 or 2.00 M $NaClO_4$.

Solutions of $pH = 4.00 \pm 0.01$ (0.05 M potassium biphthalate, Fisher) and $7.00 \pm 0.01$ (0.05 M $KH_2PO_4$, Fisher) buffers were used to calibrate the electrode system. Solutions of bases were standardized by potassium acid phthalate, KHP, titration. Prior to use, KHP was dried at 100°C for at least 2 h and cooled in the dessicator over silica gel.

### 2.2. Extraction solutions

Solutions of $NaClO_4$ and ligands (30 mM $Na_3H_3CHHS$ + 0.82 M $NaClO_4$, 0.001 M $Na_3H_3CHHS$ + 0.94 M $NaClO_4$) were prepared in doubly deionized water and the pH of the solution adjusted by addition of small volumes of saturated $CO_2$-free NaOH and 2.3 M $HClO_4$ solutions. The 2.3 M $HClO_4$ was made by dilution of 60% $HClO_4$ (Fischer) in doubly deionized water.

Stock solutions of $(HDEHP)_2$ (Sigma) in xylene (0.2 M) were prepared and stored in contact with 1.00 M $NaClO_4$ solution with pH 3.00 to extract any polyphosphate and to reach equilibrium of the reaction:

$$(HDEHP)_{2org} + Na^+_{aq} = Na(HDEHP)_{2org} + H^+_{aq}. \qquad (1)$$

Aliquots of the stock solution were withdrawn, diluted with xylene and the new solutions equilibrated by contact with 0.003 M $Na_3H_3CHHS$ + 0.82 M $NaClO_4$ solution whose pH was adjusted to the necessary value.

The $^{243}Am$ and $^{152,\,154}Eu$ stock solutions (Oak Ridge National Laboratory) were diluted in 0.001 M HCl to have a final activity of 2500 cpm/10 μL.

For the laser experiments, the pcH (= −log $H^+$ concentration) of the stock solution was adjusted by addition of aliquots of concentrated solutions of NaOH or $HClO_4$. The solutions were stirred vigorously for 30 min to allow the pcH to equilibrate. When the pcH stabilized, 8 mL of the solution were withdrawn and filtered through 0.45 μm filter (Corning) for use in the spectroscopic experiments.

### 2.3. Equipment

The titration of $H_6CHHS$ in different background electrolytes was performed with an Accumet 950 manual titrator or an ABU 90/Autoburette ("Radiometer Copenhagen") automatic titrator connected to an IBM computer. A Corning SemiMicro Combination H electrode filled with NaCl solution (rather then KCL) was used. When the solution containing $N(CH_3)_4^+$ cations was titrated, the electrode was filled with 1.00 M $(CH_3)_4Cl$ to ensure that the compositions of the solutions outside and inside the electrode were similar. Calibration of the electrode was done by measurement of the pH reading of solutions of $1.00 \times 10^{-4}$–$1.00 \times 10^{-2}$ M $HClO_4$ solutions in 1.0 M $NaClO_4$ in a $CO_2$ free cell. The relation between pH (meter reading) and pcH was determined to be

$$pcH = 0.88(\pm 0.01)pH + 0.56(\pm 0.01). \qquad (2)$$

For the solvent extraction experiments, aliquots of aqueous and organic solutions in 20 mL extraction vials were mixed in a thermostatically controlled water bath equipped with a Polystat Circulator (Cole-Palmer). Radioactive counting was done with a LS-500 TA (Beckman) liquid scintillation counter using Ecolume solution. Measurements of the stability constants were performed at 0°C, 25°C, 40°C and 60°C.

The pumped dye laser system for the spectral experiments has been described previously [4, 5].

### 2.4. Data treatment

The least-squares fit for the determination of the stability constants was performed using the Quattro Pro 6.0 program, modified for the titration data. The differences between the apparent dissociation constants for the solutions containing $Na^+$ and $N(CH_3)_4^+$ were used to estimate the complexation of $Na^+$ with CHHS ligands (on the assumption that $N(CH_3)_4^+$ is not complexed by the ligand).

The $1/D$ values versus the corresponding $[L]$ values were analyzed by regression analysis and the slope used to calculate the 1 : 1 stability constant, $K^{app}$. The reported values are the average of duplicate experiments. The error in determination of $K^{\mathrm{app}}$ from the duplicate extraction experiment was calculated from the weighted average of the $K^{\mathrm{app}}$ values $+0.02$ (the estimated error in the counting data of the radioactivity).

The "apparent" stability constants, $K^{\mathrm{app}}$, express the relationship

$$K^{\mathrm{app}} = \sum f_{\mathrm{H}_n\mathrm{L}} K_{\mathrm{MH}_n\mathrm{L}}, \tag{3}$$

where $f_{\mathrm{H}_n\mathrm{L}}$ is the concentration of the $\mathrm{H}_n\mathrm{L}$ ($n = 0-5$) species in solution and $K_{\mathrm{MH}_n\mathrm{L}}$ is the "partial" stability constant for the species Eu $\mathrm{H}_n\mathrm{L}$. The concentration values of $\mathrm{H_nL}$ were calculated from the p$Ka_n$ values for CHHS or mellitic acids. The resolution of the apparent stability constants using Corel Quattro Pro 8.0 has been described in Ref. [6].

Regression analysis for $\Delta G$ (calculated from the $K_{\mathrm{MH}_n\mathrm{L}}$ values) versus $T$ (from 0°C to 60°C) was used to calculate the enthalpy, $\Delta H$, and entropy, $\Delta S$, values; the errors in the log $K_{\mathrm{MH}_n\mathrm{L}}$ values were used to estimate the errors in $\Delta G$, $\Delta H$ and $\Delta S$.

The laser system was calibrated periodically by measuring the spectrum of 0.10 M $\mathrm{Eu(ClO_4)_3}$. The value of the maximum of the excitation peak was used to calculate the coordination numbers of Eu(III) in its complexes. To obtain the hydration number of Eu(III), the decay intensity was measured at the wavelength corresponding to the excitation maximum for the Eu(III) complexes as a function of time. A least-squares fit of intensity versus time was used to obtain the luminescence decay constant. Luminescence intensities were measured by applying a laser pulse at the wavelength of maximum absorption and measuring the luminescence intensity as a function of time. Typically, 1000 laser pulses were applied and the average relative intensity of the emitted light versus time was used to calculate the decay constant. To determine that the measured intensities were not due to hydrolyzed Eu(III) or its carbonate complexes, a solution with initial concentrations of $[\mathrm{Na_2CO_3}] = 1.0 \times 10^{-4}$ M, [Eu(III)] $= 4.4 \times 10^{-5}$ M, $[\mathrm{NaClO_4}] = 1.0$ M was prepared and its pcH adjusted to 11.0. When a precipitate was formed, the solution was allowed to stand for 1 day, filtered and the spectrum recorded. The spectrum was indistinguishable from noise, indicating that neither free europium nor its carbonate complex were present in detectable amounts in the alkaline solutions.

The excitation spectra were measured at 0.50 $\mathrm{cm^{-1}}$ increments with 50–100 pulses per point. The peaks in the spectra of Eu were deconvoluted into Lorentzian, Gaussian and Lorentzian–Gaussian product functions [7] by non-linear least-squares procedures. The Gaussian analysis gave the best approximation of the peak shape. Consequently, a Gaussian or a linear combination of a double Gaussian analysis was used to find the peak maxima by the equation:

$$\begin{aligned} Y_{\mathrm{calc,Gaus}} = {} & Y_{\mathrm{max}\ 1} \exp\{-0.5[(X - v_1)/2\sigma_1]^2\} \\ & + Y_{\mathrm{max}\ 2} \exp\{-0.5[(X - v_2)/2\sigma_2]^2\} \\ & + c + cX. \end{aligned} \tag{4}$$

In this equation, $X$ is the wavenumber, $Y$ the intensity, $v$ the wavenumber of the peak maximum, $\sigma$ the half-width, $b$ the correction for background, and $c$ the correction for the slope of the plot.

The corresponding values of $v_1$ and $v_2$ were used to estimate the coordination number, $\mathrm{CN_L}$, of the Eu(III)-ligand binding using an empirical relation [4]:

$$\mathrm{CN_L} = 0.237\ \Delta v + 0.628, \tag{5}$$

where $\Delta v$ is the difference in wavenumber of the maxima of the excitation curves of the completely hydrated and of the complexed europium cations. The decay lifetimes of the Eu(III) complexes were obtained by a least-squares analysis of the exponential fit of the relationship [5]:

$$n(\mathrm{H_2O}) = 1.05\ k - 0.7, \tag{6}$$

where $k$ is the reciprocal of decay halflife expressed in $\mathrm{ms^{-1}}$, and $n(\mathrm{H_2O})$ is the hydration number of Eu(III).

## 3. Results

The values of p$Ka_n$ obtained for CHHS are listed in Table 1. The differences in the values of p$Ka_2$ for $\mathrm{H_2CHHS^{-4}}$ in Table 1 measured in $\mathrm{NaClO_4}$ and in NaCl solutions (ca. $9.65 \pm 0.04$) versus that measured in $\mathrm{N(CH_3)_4Cl}$ indicates a degree of binding of $\mathrm{Na^+}$ to the $\mathrm{H_2CHHS^{-4}}$ anion. The value calculated for the stability constant for formation of $\mathrm{NaH_2CHHS^{-3}}$ was log $K_{\mathrm{NaH_2L}} = 1.40 \pm 0.06$. Fig. 3 are the speciation diagrams as a function of pcH for $\mathrm{H}_n$CHHS and $\mathrm{H}_n$Mel. Both $\mathrm{H_3CHHS^{3-}}$ and $\mathrm{H_3Mel^{3-}}$ are stable over larger ranges of pcH than the other protonated species, reflecting that H-bonding has utilized all 6 carboxylate groups in these anions for enhanced stability.

Table 1
Values of $\mathrm{pKa}_n$; $I = 1.0$ M

| $n$ | CHHS | | | Mellitic[a] |
|---|---|---|---|---|
| | $\mathrm{NaClO_4}$ | $\mathrm{NMe_4Cl}$ | NaCl | $\mathrm{NaClO_4}$ |
| 1 | — | — | — | 5.13 |
| 2 | $9.67 \pm 0.04$ | $11.8 \pm 0.03$ | $9.63 \pm 0.03$ | 4.20 |
| 3 | $8.05 \pm 0.02$ | $9.36 \pm 0.03$ | $7.95 \pm 0.03$ | 3.40 |
| 4 | $3.06 \pm 0.02$ | $3.07 \pm 0.03$ | $2.92 \pm 0.03$ | 2.24 |
| 5 | $2.53 \pm 0.01$ | $2.53 \pm 0.03$ | $2.33 \pm 0.03$ | 1.50 |
| 6 | $2.07 \pm 0.03$ | $1.90 \pm 0.03$ | $1.89 \pm 0.03$ | 0.63 |

[a] Interpolated from values at $I = 0$, 0.1 and 3 M ($\mathrm{NaClO_4}$).

Table 2
Values of apparent stability constants for Eu(III). $I = 1.0$ M ($NaClO_4$)

| Ligand | pcH | p*K*a | log $\beta$ | $\Delta H$(kJ/M) | $\Delta S$ (J/M/K) |
|---|---|---|---|---|---|
| Phthalate | — | 7.38 | 3.84 (0.1 M)[a] | 10.4 | 108 |
| Hphthalate | — | 2.51 | 2.21[a] | — | — |
| Hmel | — | — | 5.41[a] | 19.9±2.5 | 173±9 |
| $H_2$Mel | 5 | 6.41 | 5.01[b] | — | — |
| $H_3$Mel | 3.5 | 5.73 | 3.43[b] | — | — |
| $H_4$Mel | — | 3.52 | 2.44[b] | — | — |
| HMA[c] | — | — | 5.08 | 14.4 | 154 |
| PMA[d] | — | — | 5.02 | 14.9 | 147 |
| TMA[e] | — | — | 4.45 | — | — |
| $H_nCHHS$ | 3.00 | 8.05 | 1.83±0.02[c] | 16.8±0.9 | 98±3 |
| $H_nCHHS$ | 4.00 | 3.06 | 2.07±0.02[c] | 9.3±1.0 | 67±3 |

[a] Ref. [7].
[b] Obtained by reanalysis of data in Ref. [10].
[c] HMA = hemimellitic acid, 1, 2, 3-benzyltricarboxylic acid.
[d] PMA = pyromellitic acid , 1, 2, 4, 5-benzyltetracarboxylic acid.
[e] TMA = trimellitic acid, 1, 2, 4-benzyltricarboxylic acid.

Attempts to determine the stability constants for $MH_nCHHS$ complexation using potentiometric titration failed because of formation of insoluble products. The formation of these products was a kinetically slow process. When NaOH was added to the solution containing 0.005 M $H_6CHHS$ + 0.005 M $Nd^{3+}$ + 0.100 M $HClO_4$, precipitation began when the pcH approached 2; the pcH continued to increase as the titration and resultant precipitation proceeded. As a result, the stability constant could not be determined by this method in the acidic region. The precipitate redissolved at pcH ~ 9.0. In the titration, 7.0 equivalents of NaOH were used for each equivalent of $H_6CHHS$, consistent with a Nd : CHHS : $OH^-$ ratio of 1 : 1 : 1, indicating the formation of a complex with the formula $NdCHHS(OH)^{4-}$.

The stability constants for Eu(III)-$H_nCHHS$, for Eu(III)-mellitate, for Eu(III)–CHHS and for Eu(III) 1 : 1 complexation with 1,2,3-, 1,2,4-, 1,2,4,5-benzene-polycarboxylic and phthalic acids are listed in Table 2. Values reported for the entropy and the enthalpy of formation are listed also if available. The values of $\beta^{app}$ for the Eu-Mel and EuCHHS complexes are plotted in Fig. 1. The p$Ka_n$ values are plotted in Fig. 2 (for 1.0 M ($NaClO_4$) solution). The calculated coordination number, $CN_L$, for Eu(III) in the CHHS and mellitate complexes as a function of pcH are shown in Fig. 3.

## 4. Discussion

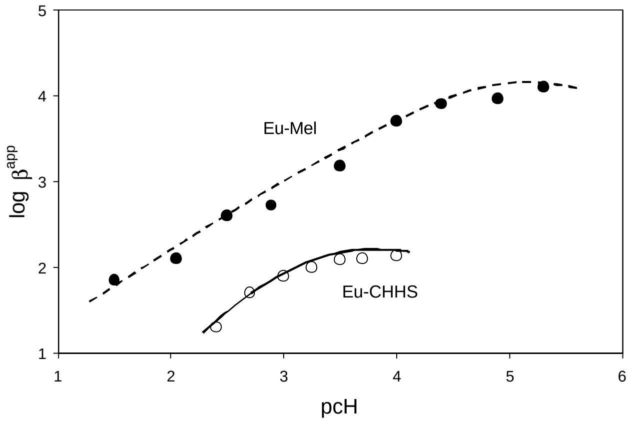

Fig. 1. Plots of log $\beta^{app}$ versus pcH for Eu-mellitate (-○-) and Eu-CHHS (-•-).

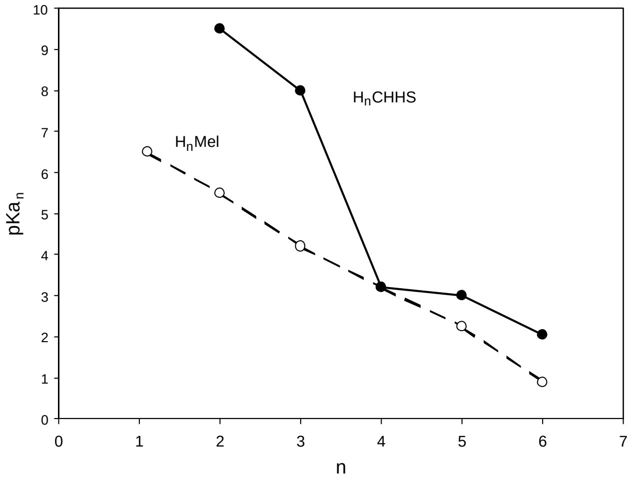

Fig. 2. Plots of p$Ka_n$ versus pcH for mellitic acid (-•-) and cyclohexylhexacarboxylic acid (-○-).

A measure of the effect of the flexible cyclohexyl structure versus the rigid benzene structure is seen in the difference in complexation of the tricarboxylate ligands of these two systems. The hemimellitate (1, 2, 3-tricarboxylate) was reported to have a stability constant, log $\beta_{101}$ of 5.08, and an entropy value, $\Delta S_{101}$, of 154 J/M/K [2]. The complex of Eu(III) with pyromellitate (1, 2, 4, 5 tetracarboxylate) has a very similar stability constant and almost the same entropy value for complexation [2]. The complex of Eu(III) with phthlate (1,2-dicarboxylate) has a stability constant and an entropy value slightly less than these [7]. However, this difference can be accounted for by the statistical effect of having multiple bidentate sites on the tri- and tetracarboxylates in contrast to the single bidentate site of the phthlate ligand. The agreement of the data is strong evidence that the chelation with the tri- and tetracarboxylates is bidentate, involving two adjacent carboxylates of the ligand.

To supplement the thermodynamic values available for the 1, 3, 5-cyclohexyltricarboxylate ligand, we have measured the coordination number of the ligand from the shift in the luminescent emission spectrum and the hydration number of the complex from the halflife of the florescent decay. The spectra of solutions in the range of

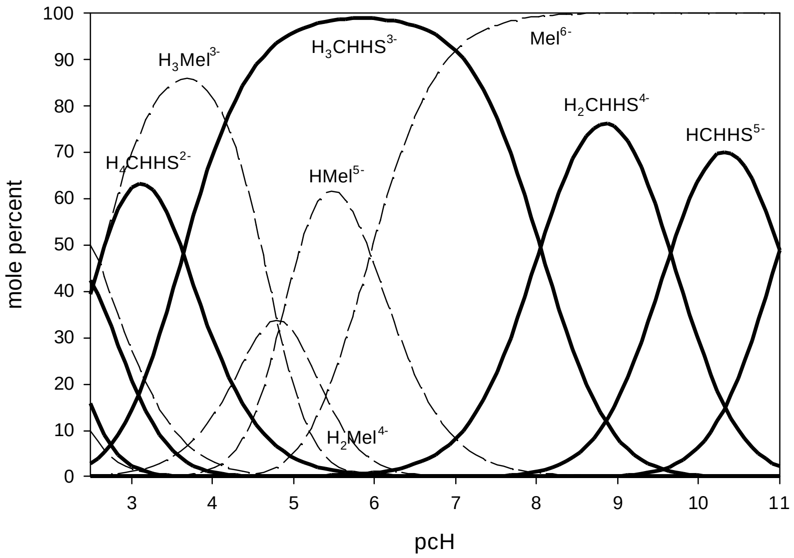

Fig. 3. Plot of concentration of $H_nL$ species as a function of pcH for CHHS and mellitate.

pcH 2.5–7.0 had only a single peak with a maximum centered around $17271.9 \pm 0.9\,cm^{-1}$ which corresponds to a ligand coordination number of $1.1 \pm 0.2$. The absorption maximum for hydrated Eu(III) had a value of $17272.3\,cm^{-1}$. Although the values were scattered due to weak signals, the average value of the hydration number of Eu(III), calculated from repeated measurements of the luminescent lifetime, was equal to $7 \pm 1$. This agrees with molecular modeling which indicates that carboxylate groups in the 1,3,5-triacid anion are oriented to near-equitorial positions and the complex involves bonding of a single carboxylate group to Eu(III). The 1,3,5-triacid has been reported to have mondentate behavior in complexes with other cations such as $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ [8]. Apparently, the Coulombic and Van der Waals repulsive interactions are of sufficient strength in the conformers of the 1,3,5-triacid anions that the carboxylate groups are held sufficiently apart that the 8-membered chelate ring for a bidentate complex is too weak to be significant.

Analysis of the solvent extraction data gave the following stability constants of $EuH_nCHHS$ complexation:

(a) for formation of $EuH_3CHHS$, $\log \beta_{131} = 2.17 + 0.03$,
(b) for formation of $EuH_4CHHS^+$ $\log \beta_{141} = 1.33 + 0.36$.

The errors are 95% confidence limits. At pcH = 3.0, $H_4CHHS^{4-}$ is the dominant anion (Fig. 3) with $H_5CHHS^{1-}$ and $H_3CHHS^{3-}$ present at about 30% of the $H_2CHHS^{4-}$ concentration and at pcH 4.0, $H_3CHHS^{3-}$ and $H_4CHHS^{2-}$ are present in about equal concentrations. $H_3CHHS^{3-}$ is the dominant species from pcH 4–8. The $K^{app}$ values in Table 2 are consistent with $EuH_3CHHS^0$ being the dominant species between pcH 3.5 and pcH 8.

The spectral measurements of the CHHS complexes yielded ligand coordination numbers which increased to ca. 2 at pcH 4, decreased to a minimum of ca. 0 at pcHs between 5.5 and 6.5, and increased to 2 by pcH 8 (Fig. 4). Above pcH 8, $CN_L$ further increased to a value of 7 ($\pm 0.5$) by pcH 10. The changes from pcH 8–10 in the spectra are shown in Fig. 5. The value of ca. 0 in the solutions of pcH 5.5–6.5 can be attributed to formation of an insoluble bidentate chelate species in this range, presumably because the $EuH_3CHHS$ is a neutral hydrophobic species. Precipitation resulted in very weak spectra with a small peak at ca. $17\,274\,cm^{-1}$ due to uncomplexed Eu(III). As the pcH was increased to 8, the soluble species $EuH_2CHHS^+$ formed with $CN_L = 2$. At a higher pH a second kind of species with an absorption maximum centered at $17\,241\,cm^{-1}$ became predominant. The maximum corresponded to a species with $CN_L = 7$ and a hydration number for Eu(III), from the luminescence lifetime measurement, of 2.5. These data are consistent with a complex with the formula $Eu(CHHS)(OH)(H_2O)_2^{4-}$. This species was not observable at pcH ca. 8.0; however, the signal from that complex grows in importance with increased pcH and becomes predominant by pcH = 10.0. There was no further change in $CN_L$ or hydration number above pcH 10. These observations suggest the reaction:

$$EuH_2CHHS^- \bullet 6H_2O + 3OH^-$$
$$\rightarrow EuCHHS(OH)^{4-} \bullet 2H_2O + 6H_2O.$$

A hydration value of 2.5 for the complex is in agreement with 2 coordinated water molecules and one $OH^-$ group as the value ($N_{H2O}$) of 2.5 indicates 5 OH vibrations

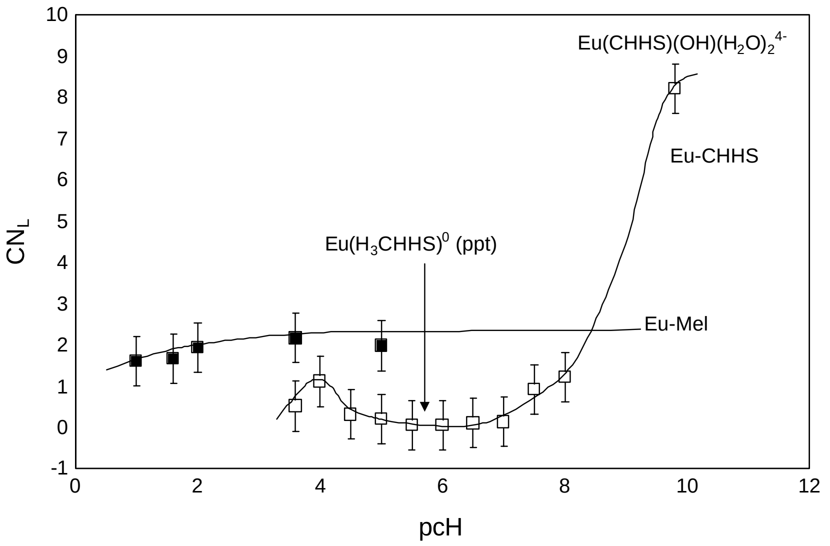

Fig. 4. Variation of the ligand coordination number versus pcH for Eu + CHHS and Eu-mellitate.

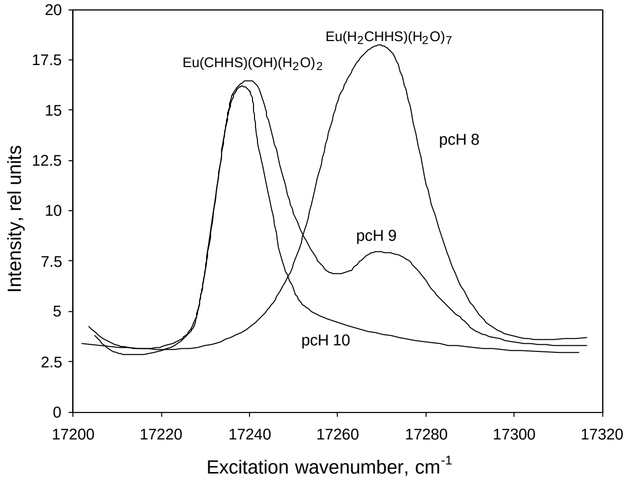

Fig. 5. Excitation spectra of Eu-$H_n$CHHS$_n$ at pcH 8, 9 and 10.

quenching the Eu(III) luminescence [9]. The value of $CN_L = 7 \pm 0.5$ suggest 6–8 Eu-ligand bonds involving the carboxylate oxygens. At pcH 10, the dominant anion is $HCHHS^{5-}$, which results in 5 carboxylate groups available for bonding. This plus the 3 oxygen donors from the 2 $H_2O + 1\ OH^{1-}$ gives a total CN(Eu) = 8, a common total coordination number for Eu in complexes.

The Ln(III)-mellitate complexation had been studied previously [10]. The data were reanalyzed with a computer program [11] not available at the time of the study. The $\beta^{app}$, p$Ka_n$ and $CN_L$ values obtained in the new analysis of the data are shown in Table 2 and Figs. 1–4. We also measured the Eu-mellitate system by laser luminescence to obtain the $CN_L$ and $n(H_2O)$ values as a function of pcH. The mellitate values in Table 2 are the "resolved" constants $EuH_3Mel$ and $EuH_4Mel$ (3.34 and 2.42) and can be compared to the resolved values for the $EuH_3CHHS$ and $EuH_4CHHS$ listed previously of 2.17 and 1.33. In all four complexes, the binding was bidentate. The larger values for mellitate complexation are consistent with increased charge on the carboxylate donors via polarization of the pi electron density in the benzene ring.

The difference in the ring flexibility is most obvious in the speciation with increased pcH. Due to the rigid benzene "backbone" in mellitate, the carboxylates can form only bidentate structures as shown by the constancy of the $CN_L = 2$ over the entire pcH range studied. By contrast, Eu-CHHS binding was bidentate at lower pcH values but as the carboxylate groups were deprotonated by increasing pcH, the complex, Eu $(HCHHS)(OH)(H_2O)_2^{3-}$ was formed with a $CN_L$ of $7 \pm 1$. This must involve a contorted boat structure of the cyclohexyl ring to allow coordination of the 5 deprotonated carboxylate groups. It is also possible that the CHHS anion is fully deprotonated in the complex as 7 equivalents of NaOH were required to reach pcH 10–11. In that case, Eu(III) may bind to all 6 carboxylate groups for $CN_L = 6$ plus 3 more coordination sites occupied by the lone $OH^-$ and the two waters. This would result in a total $CN_T$ of 9 which is also observed for many Eu(III) complexes.

In summary, the 1, 3, 5-cyclohexaltricarboxylate binds Eu(III) by a single carboxylate site due to the distance between the carboxylate groups as a result of the boat conformation. The hemimellitate, trimellitate and pyromellitate anions formed bidentate complexes as did mellitate. This was independent of the protonation of the $EuH_nMel$ complexes for $n = 0-4$. The cyclohexylhexacarboxylate complexes, $EuH_nCHHS$, were bidentate to ca. pcH 8 above which the contorted boat structure of the cyclohexyl ring allowed coordination of multiple carboxylate groups, leading to the complex $\mathrm{Eu(HCHHS)(OH)(H_2O)_2^{-3}}$.

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