

Mixed Ligand Complexes of Some Lanthanides with EDTA as Primary Ligand & Malic or N,N-Hydrazinediacetic Acids as Secondary Ligands

SAMIR A ABOU ALI*, NABIL A IBRAHIM, GAMAL B MOHAMED & MOHAMED K EL-DEEB

Chemistry Department, Faculty of Science and Education, Alexandria, Egypt

Received 14 February 1984; revised and accepted 3 July 1984

The acid dissociation constants of malic acid (H_2L) and N,N-hydrazinediacetic acid (H_2Z) and the formation constants of their mixed ligand complexes with lanthanides and EDTA have been determined potentiometrically in 0.1 M KNO_3 and $30 \pm 0.1^\circ C$. Malic acid is found to act as a monodentate ligand in the ternary complexes while N,N-hydrazinediacetic acid acts as a bidentate ligand.

Mixed ligand complexes of rare earth metal ions with complexons and dicarboxylic acids have generated interest because of their importance in the ion exchange separation of lanthanide mixtures with mixed eluents¹⁻⁴.

The present work deals with the study of the mixed ligand complexes of some lanthanides with EDTA as the primary ligand and N,N-hydrazinediacetic acid (H_2Z) or malic acid (H_2L) as a secondary ligand.

Reagent grade chemicals were used. Stock solutions of rare earth nitrates were prepared from the corresponding oxides (BDH) and standardized as usual⁵. N,N-Hydrazinediacetic acid (Moscow Chemical Factory, Vikova) was purified by dissolving it in ammonia. The filtrate was acidified with dil. HCl to pH 1.8 and the precipitate formed washed with water and dried *in vacuo* over P_2O_5 . Stock solutions of all the ligands were standardized potentiometrically.

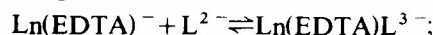
pH measurements were performed using a Beckman model 4500 digital pH-meter (accuracy ± 0.002 pH units). The pH and conductances were measured under nitrogen at $30 \pm 0.1^\circ C$.

The pK of the secondary ligands have been determined by potentiometric titration of ligand solutions (5×10^{-3} M). The titration curve of malic acid shows one sharp inflection at $a = 2$ (a is the number of mol base added per mol of the ligand) indicating simultaneous neutralization of the two carboxylic protons of the ligand. The overlapping pK values obtained using the equations described earlier⁶ are $pK_1 = 3.298 \pm 0.084$ and $pK_2 = 4.772 \pm 0.082$. The titration curve of N,N-hydrazinediacetic acid shows two separate sharp inflections at $a = 1$ and $a = 2$,

indicating the stepwise neutralization of the two protons. The pK values obtained employing equations reported earlier⁷ are: $pK_1 = 3.203 \pm 0.021$ and $pK_2 = 7.128 \pm 0.023$.

The stoichiometric composition of the mixed ligand complexes is found to be 1:1:1 by conductometric measurements.

The stability constants ($\log K_f$) of the lanthanide complexes with malic acid⁸ and with N,N-hydrazinediacetic acid⁷ are much smaller than those of $Ln(EDTA)^-$ (ref. 9). The formation of the mixed ligand complexes probably proceeds as follows:



$$K_f = [Ln(EDTA)L^{3-}] / [Ln(EDTA)^-][L^{2-}]$$

The equilibrium concentration of all species present have been calculated as given in literature^{1,10}. The $\log K_f$ values are listed in Table 1.

In the case of $Ln^{3+} - EDTA - H_2L$, the values of $\log K_f$ vary between 1.81 and 2.32. The values of $\log K_f$ of the binary complexes of lanthanide ions with malic acid are in the range 3.96 to 4.98 (ref. 8), and the values of $\Delta \log K$ ($\log K_1 - \log K_f$) vary from 2.45 to 2.79, indicating that malic acid acts as a monodentate ligand in the ternary complexes. Thus, malic acid coordinates in the mixed ligand complexes through the oxygen atom of one of the $-COOH$ groups, while the $-OH$ group remains free.

The $\log K_f$ values for $Ln^{3+} - EDTA - H_2Z$ system vary from 2.13 to 3.29. These values are nearly half of $\log K_1$ values for LnZ^+ , where (in the binary complexes) two chelate rings are formed⁷. The $\Delta \log K$

Table 1—Formation Constants of Mixed Ligand Complexes ($\log K_f$) for the Systems $Ln^{3+} - EDTA - H_2L$ and $Ln^{3+} - EDTA - H_2Z$

[Temp = $30 \pm 0.1^\circ C$, $\mu = 0.1$ M(KNO_3)]

Ln^{3+}	$\log K_f$ for system	
	$[Ln(EDTA)L^{3-}]$	$[Ln(EDTA)Z^{3-}]$
La	—	2.439 \pm 0.244
Pr	1.816 \pm 0.009	2.902 \pm 0.094
Nd	2.014 \pm 0.021	2.872 \pm 0.053
Sm	2.137 \pm 0.024	2.978 \pm 0.030
Eu	2.247 \pm 0.014	3.099 \pm 0.027
Gd	2.325 \pm 0.008	3.195 \pm 0.047
Tb	2.146 \pm 0.017	2.922 \pm 0.107
Dy	2.128 \pm 0.012	2.542 \pm 0.031
Ho	1.984 \pm 0.017	2.357 \pm 0.147
Er	2.140 \pm 0.012	2.128 \pm 0.097
Tm	1.982 \pm 0.013	2.143 \pm 0.063
Yb	1.945 \pm 0.016	2.156 \pm 0.109

values ($1/2 \log K_1 - \log K_f$) for this system range from 0.05 to 0.70. So, only chelate ring is formed in the mixed ligand complexes of the type $\text{Ln}(\text{EDTA})\text{Z}^{3-}$. Thus, N,N-hydrazinediacetic acid behaves as a bidentate ligand bonding through one of the oxygen atoms of the carboxylic groups and the nitrogen atom, β to the carboxylic groups.

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