TABLE I. The formation rate constants of the Lnedta complexes and the k_{CeY}^{Ln} values.

k $(M^{-1} s^{-1})$	Nd	Gd	Er	Y
$10^8 \times k_{HY}^{Ln}$	2.7	3.0	1.8	0.9
$10^6 \times k_{H_2Y}^{Ln}$	1.1	1.1	0.54	0.18
k_{CeY}^{Ln}	0.35	0.28	0.22	0.14

of the reaction taking place by the direct attack of the Ln^{3+} ions on the protonated complex CeHedta has some importance only in the reaction with Y^{3+} ($k_{CeHY}^{Y} = 200 \ M^{-1} \ s^{-1}$). The rate constants obtained are listed in Table I.

If the formation of complexes takes place by the Eigen-mechanisms, the second-order rate constants can be expressed as the product of the water-exchange rate constant of the metal ion and the outer sphere association constant K_{os} of the ions: $k_{HY}^{Ln} = k_{Ln}^{-H_2O} \times K_{os}$. The water-exchange rate constants of the $Ln^{3+} \cdot aq$ ions are quite uncertain but their order of magnitude is about 10^8 [6]. A more accurate value is known for the $Gd^{3+} \cdot aq$, $k_{Gd}^{-H_2O} = 10 \cdot 6 \times 10^8 \ s^{-1}$ [8]. Taking into account the value $k_{HY}^{Gd} = 3 \times 10^8 \ M^{-1} \ s^{-1}$ (Table I) the association constant K_{os} can be calculated as $K_{os} = 0.28 \ M^{-1}$. For 3+ and 3− ions the predicted K_{os} value is about 100, that is much higher [9]. This suggests that the formation rate constants obtained are too low to assume the rate determining role of the water-exchange from the first coordination sphere. It seems more probable that the rate controlling step in the reaction between the Ln^{3+} ion and the monoprotonated Hedta^{3-} ligand is the ring closure because one of the iminodiacetate groups of the ligand is deprotonated. The $k_{H_2Y}^{Ln}$ values are about 2 orders of magnitude lower than the k_{HY}^{Ln} values which can be interpreted assuming a slower, rate controlling proton transfer step (or deprotonation) making possible the coordination of a deprotonated iminodiacetate group.

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A31

About Some Mixed Molecular Complexes of the Dithiooxalate Anion with Lanthanides and Some Transition Elements
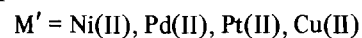
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The dithiooxalate anion, $S_2C_2O_2^{2-}$, has been previously shown to give low dimensional compounds, such as:

$$M = Ca, Ba, Zn, Mn(II)$$
$$MM'(S_2C_2O_2)_2 \text{ with}$$
$$M' = Ni(II), Pd(II), Pt(II), Cu(II)$$
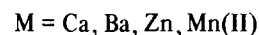
A particular interest has been afforded to the compound with $M = Mn$, $M' = Cu$, because of its one-dimensional structure constituted of ordered extended chains, $-Mn-L-Cu-L-Mn-$ ($L = S_2C_2O_2$); and moreover because of its very interesting magnetic properties.

The substitution of lanthanide elements (Ln(III)) to the metal M, led to a new family characterized by a structural entity:

$$Ln_2(Solvent)_{2n}M'_3(S_2C_2O_2)_6$$
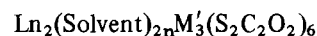
i.e. a neutral centrosymmetric heteropentanuclear unit.

This family has been particularly studied for $M' =$ Ni, Solvent $= H_2O$, and Ln(III) = La, Ce, Nd, Sm, Eu, Gd, Y, Dy, Er, Yb. Within this series a modification of the lanthanide environment occurs between Dy and Er. The coordination polyhedron is a tricapped trigonal prism (CN = 9, n = 5) for the bulkiest lanthanides while it is only a bicapped trigonal prism (CN = 8, n = 4) for the other lanthanides. The loss of one water molecule in the coordination sphere of the lanthanide can be attributed to steric effects in relation with the decrease of the lanthanide radius. The CN modification induces a rearrangement of the ligand ($O_2C_2S_2$) around the lanthanide, and a change of structure. Bulkiest lanthanides, up to Dy, crystallize in the monoclinic system (P2$_1$/c) and their lattice looks like a channels structure with inserted water molecules within the channels; while the less bulky lanthanides crystallize in the triclinic system

(PĪ) with a lattice comparable to a pseudo-lamelar structure, intercalated water molecules occupying the interlayer spaces.

The substitution of Pd, Pt, Cu to Ni (with Ln = Eu) gives rise to isostructural compounds.

Change of solvent (Solvent = $(CH_3)_2SO$) does not modify the geometry of the neutral centrosymmetric heteropentanuclear entity, dmso molecules substituting to water molecules. Compounds obtained with M' = Ni, Ln = Ce, Eu, Er crystallize in the triclinic system (PĪ), with CN = 9, n = 5.

A32

Synthesis and Structure of Uranyl Complexes with Carboxylic Acids and Oxygen Containing Neutral Ligands

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Complexes $[UO_2AC_2CH_3CON(CH_3)_2]_2$, $[UO_2(C_6H_5COO)\cdot 2(CH_3)_2SO_2]$ and $[UO_2AC_2\cdot 1.5CO(NH_2)_2]$ were obtained by the interaction of the aquadiacidouranyl complexes with the neutral ligands.

Single crystal X-ray diffraction studies show that $[UO_2Ac_2CH_3CON(CH_3)_2]_2$ has dimeric structure and uranyl ion here is pentacoordinated. Crystal structure of the $[UO_2(C_6H_5COO)_2\cdot 2(CH_3)_2SO)]$ is built of monomeric complexes where uranyl ion is hexacoordinated, and structure of the $[UO_2Ac_2\cdot 1.5CO(NH_2)_2]$ is formed by the isolated complex $[UO_2Ac_2\cdot 3CO(NH_2)_2]^+$ cations and $[UO_2Ac_3]^-$ anions. Complex $[UO_2Pr\cdot 1.5CO(NH_2)_2]$ is built in the same way, uranyl ions are penta- and hexacoordinated. The uranyl complex with dicarboxylic succinic acid and DMSO $[UO_2COOCH_2CH_2COO\cdot (CH_3)_2SO]$ is built of chains where each acidoligand is bound in a bidentate way to one pentacoordinated uranyl ion, forming 4-membered cycle, and in a monodentate way to two other pentacoordinated uranyl ions. The crystal structure of the $NH_4[UO_2Pr_3]$ is built of isolated complexes, each bidentate propionate ion forms a 4-membered cycle. The growth of the chains of monocarboxylic acids leads to predominance of the isolated forms of uranyl complexes.

A33

Equivalent Conductivities and First Hydrolysis Constant Determination of Aqueous Trivalent Lanthanide Ions by Conductance Data Fitting
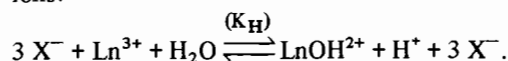
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Conductance measurements by Spedding *et al.* [1] were obtained with halide solutions at pH $\cong$ 6.4 without taking into account hydrolysis of M^{3+} ions:

$$3\,X^- + Ln^{3+} + H_2O \overset{(K_H)}{\rightleftharpoons} LnOH^{2+} + H^+ + 3\,X^-.$$

Since the aqueous solution should contain several ions (and small quantities of carbonate) we developed [2] a generalized Robinson-Stokes equation which is applicable to mixture of ions. Therefore observed equivalent conductivities can be derived as:

$$\Lambda_{obs} = \Lambda^o_{obs} - \frac{\{2A'I + B'\Lambda^o_{obs}\sum_p (S^p)^2(1-\sqrt{q_p})\}\sqrt{1}}{1 + Ba\sqrt{I}}$$

(1)

with $\Lambda^o_{obs} = (\sum_i C_i|Z_i|\lambda^o_i)/3C$; $A' = A/3\,C$; $A = 30.32$; $B' = 0.7852$; I: ionic strength; C_i and Z_i: concentration and charge of 'i' ion; S^p and q_p are eigen vectors and eigen values of the Onsager–Kim matrix.

Taking into account hydrolysis, eqn. (1) is linearized and we fitted the experimental conductance data. The agreement between calculated and experimental data is 0.2%.

We deduce the first hydrolysis constant (log $K_H \cong$ 7) and values of the hydrated radius for 13 lanthanides and we will consider the variations of these interesting parameters along the 4f series. Moreover the obtained limiting equivalent conductivities λ_o are 5% less than those which are generally tabulated.

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