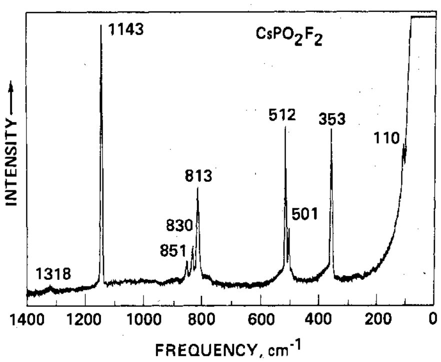

Figure 2. Raman spectrum of solid $CsPO_2F_2$ recorded at 25 °C with a spectral slit width of 5 cm^{-1}.

acteristic HF signal at ϕ 193. The assignment of the ϕ −33 signal to SO_3F^- was verified by recording the spectrum of $CsSO_3F$ in HF under the same conditions.

In view of the above-mentioned usefulness of NF_4^+ salts of oxyanions for the preparation of novel hypofluorites, it appeared interesting to attempt the syntheses of $(NF_4)_2SO_4$ and $NF_4PO_2F_2$. The thermal decomposition of these two hypothetical salts would offer an opportunity to prepare the yet unknown hypofluorites $SO_2(OF)_2$ and $POF_2(OF)$. However, both the SO_4^{2-} and $PO_2F_2^-$ anions were found to interact with anhydrous HF according to eq 3 and 4. Attempts to prepare

$$SO_4^{2-} + 3HF \rightarrow SO_3F^- + H_2O + HF_2^- \qquad (3)$$

$$PO_2F_2^- + 4HF \rightarrow PF_6^- + 2H_2O \qquad (4)$$

$POF_2(OF)$ by fluorination of $HOPOF_2$ with atomic fluorine, generated by the controlled decomposition of $NF_4HF_2{\cdot}nHF$,[22] were also unsuccessful. The main products were NF_4PF_6[9] and an unidentified nonvolatile phosphorus oxyfluoride.

Although vibrational spectra have been reported[31-33] for the $PO_2F_2^-$ anion, the previous assignment of several fundamentals is open to question. Figure 2 and Table II summarize the vibrational spectra of $CsPO_2F_2$, obtained in our study. The given assignment was made by analogy with that of isoelectronic SO_2F_2 which is well established.[37-39] Whereas, the splitting of $\nu_8(B_2)$ can easily be explained by Fermi resonance with $(\nu_4 + \nu_9)(B_2)$, the reason for the observed splitting of ν_4 is less obvious. The possibility of one of the components assigned to ν_4 actually being due to the $\nu_5(A_2)$ torsional mode cannot be ruled out but is unlikely due to the facts that this mode should be infrared inactive under C_{2v} selection rules and usually is of such low intensity in the Raman spectra that it is very difficult to observe.

In summary, the present study shows that within the isoelectronic series ClO_4^-, SO_3F^-, $PO_2F_2^-$, SO_4^{2-}, the first two anions are capable of forming NF_4^+ salts of moderate stability which can decompose to NF_3 and the corresponding hypofluorites. The syntheses of $NF_4PO_2F_2$ and $(NF_4)_2SO_4$ by metathesis in HF were prevented by the reaction of $PO_2F_2^-$ and SO_4^- with the solvent to yield PF_6^- and SO_3F^-, respectively.

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Registry No. $NF_4^+SO_3F^-$, 74096-76-7; $CsSO_3F$, 13530-70-6; $CsPO_2F_2$, 17117-59-8; NF_4SbF_6, 16871-76-4; NF_3, 7783-54-2; $FOSO_2F$, 13536-85-1; Cs_2SO_4, 10294-54-9; $CsPF_6$, 16893-41-7.

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Peroxo- and Hydroxolanthanide(III) Complexes of the EDTA Family

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Three series of crystalline heteroligand lanthanide complexes with EDTA are reported. The new compounds have been characterized by infrared and proton NMR spectra, conductivity in aqueous solution, and powder X-ray photographs. Two of the series contain peroxides. The complexes of the type $KLnEDTA{\cdot}xH_2O_2{\cdot}yH_2O$ (x = 0.5, y = 4 for Ln = Y; x = 0.5, y = 6 for Ln = Eu, Gd; x = 2, y = 5 for Ln = La, Nd) are obtained from neutral or weakly acid solutions. Some of them are considered to be peroxo hydrates because of the easy release of peroxo oxygen. The complexes of the second type, obtained from alkaline solutions, $K_3Ln(O_2)EDTA{\cdot}yH_2O$ (y = 3 for Ln = Y; y = 6 for Ln = La, Nd) and $K_3Ln(O_2)EDTA{\cdot}xH_2O_2{\cdot}yH_2O$ (x = 1, y = 5 for Ln = Eu, Gd), contain one peroxo group which is retained on prolonged heating in vacuo, implying the presence of a coordinated peroxo ligand. The infrared spectra support this evidence by showing an additional band between 840 and 825 cm^{-1}, expected for the stretching of a coordinated peroxo group. These monoperoxo–EDTA complexes represent the first crystalline stoichiometric peroxo compounds of rare earths. Molar conductivity of these salts in water indicates the presence of 1/1 and 3/1 electrolytes, respectively, and powder photographs reveal isomorphous pairs dependent upon the degree of hydration. The third series of complexes $K_2Ln(OH)EDTA{\cdot}4H_2O$ is obtained from alkaline solutions. Molar conductivity of these salts implies the presence of 2/1 electrolytes. The proton NMR spectra show a more complex resonance pattern than the spectra of peroxo–EDTA complexes. According to powder X-ray patterns the Ln = Y, La, Eu, and Gd complexes are isomorphous.

Introduction

The peroxo derivatives of lanthanides reported to exist in the solid state so far are poorly characterized oxohydroxolanthanum(III) hydrates, containing Ln/peroxide ratios of 1/1 and 1/2. They are stable at lower temperature only, cannot be dehydrated without loss of oxygen, and decompose at room temperature.[1,2] Some spectrophotometric solution studies do

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exist.[3] An interesting 5-coordinated air-sensitive La(III) compound was also reported, revealing the presence of a doubly bidentate bridging peroxo group.[4]

Interaction of hydrogen peroxide with early transition-metal ions has been of interest to us for a long time[5] and is becoming at present more important due to its potential relation to redox processes proceeding in vivo. Biochemical aspects of electron transfer involving hydrogen peroxide may well involve the early transition-metal ions present in tissue,[6] and their participation in these bioprocesses is intriguing. Application of lanthanides in biological and medicinal chemistry has increased significantly in the last decade.[7] Several ions are used as inorganic fluorescent probes and isomorphous replacement for alkaline-earth ions in a variety of biochemical studies.[8] Toxicity and biochemical interactions of lanthanide ions in vivo are not understood. Comprehension of aqueous chemistry of lanthanide ions, coexisting with knowledge of the properties of heteroligand spheres, is needed to illuminate the interactions and the role of lanthanide ions present in living cells. The aminopolycarboxylato complexes and peroxo derivatives should be consequently scrutinized with a renewed interest. Aminopolycarboxylato–peroxo ligand combination was reported in some solution spectrophotometric studies only.[9] Heteroligand spheres involving peroxo ligands are intriguing systems, which should be able to modify the redox properties of the peroxo group. Catalysis of metal complexes in kinetics of hydrogen peroxide decomposition is an active research field,[10] and metal ions possessing the ability to form heteroligand spheres involving peroxo ligand represent a special setup, which may eventually well prove to be of biochemical significance.

Previously we have prepared and characterized a number of heteroligand peroxo complexes of M(V) = V, Nb, and Ta, which contain one, two, or three peroxo groups in combination with fluoro, oxalato, dipyridyl, *o*-phenanthroline, 8-hydroxyquinoline, and EDTA ligands.[5] It seemed plausible that lanthanide ions should form stable peroxo complexes too, if provided with a suitable heteroligand environment.[11] Our search was successful on intermixing peroxo groups with EDTA.

Experimental Section

All solvents and chemicals in the experiments were of reagent grade, obtained commercially, and were used without further purification.

Preparation of $KLnEDTA \cdot xH_2O_2 \cdot yH_2O$ (x = 0.5, y = 4 for Ln = Y; x = 0.5, y = 6 for Ln = Eu, Gd; x = 2, y = 5 for Ln = La, Nd). The lanthanum complex was prepared from the freshly precipitated hydroxide, obtained from $La(NO_3)_3 \cdot 6H_2O$ (4.6 g). Lanthanum hydroxide was heated (20 min, 60 °C) with H_4EDTA (3.0 g in 10 mL of H_2O) to obtain crystalline HLnEDTA(aq). This suspension was then reacted with an aqueous solution (10 mL) of potassium hydroxide (0.8 g), which was added dropwise until the precipitate dissolved and pH 10.2 was reached. Hydrogen peroxide (30%, 10 mL) was then added, while pH dropped to 6.7–7.0. The salt was precipitated from the clear solution by gradually adding ethanol until the mother liquid became turbid. Crystallization was enhanced by rubbing the walls of the container. Crystals obtained were filtered, dissolved in hydrogen peroxide (20%, 40 mL), and repeatedly precipitated with ethanol. They were filtered, washed with ethanol (80% and absolute, respectively), which was decanted, and air-dried; yield 50%. Analogous neodymium, europium, and gadolinium complexes were prepared similarly. For the yttrium complex the mother liquid was left standing overnight with a fivefold volume excess of ethanol. These complexes decompose on heating but are stable for months if kept in closed vials at room temperature.

Preparation of $K_3Ln(O_2)EDTA \cdot xH_2O_2 \cdot yH_2O$ (x = 0, y = 3 for Ln = Y; x = 0, y = 6 for Ln = La, Nd; x = 1, y = 5 for Ln = Eu, Gd). Lanthanum hydroxide, freshly precipitated from $La(NO_3)_3 \cdot 6H_2O$ (4.8 g) was treated with H_4EDTA (3.0 g) in water (10 mL). The mixture was heated (20 min, 60 °C) until crystalline, insoluble HLaEDTA(aq) formed. It was cooled, and hydrogen peroxide (30%, 10 mL) was added, followed by potassium hydroxide (2.8 g) dissolved in water (10 mL), which was added dropwise under stirring. The precipitate was dissolved gradually (pH ~6), and a clear solution was obtained. To it was added an aqueous solution of potassium hydroxide to reach pH 13.5. The reaction mixture was then treated with more hydrogen peroxide (30%, 10 mL), and pH dropped to about 10. The clear solution was left standing for about 15 min, and then ethanol was poured into it quickly (six- to sevenfold volume excess). Needle-shaped crystals appeared. They were filtered, washed twice with 96% and 100% ethanol, respectively, and air-dried; yield 60%. Yttrium, neodymium, europium, and gadolinium complexes were prepared similarly, the mother liquid with added ethanol being left standing for 6–7 h for yttrium. The crystals of all the complexes can be dehydrated in vacuo over P_2O_5 at 110 °C. Anhydrous substances of all these lanthanides become hygroscopic and, left in air, promptly absorb water.

Preparation of $K_2Ln(OH)EDTA \cdot 4H_2O$ (Ln = Y, La, Nd, Eu, Gd) was similar for all the ions, and that of the lanthanum complex is described as an example. The hydroxide, freshly prepared from $La(NO_3)_3 \cdot 6H_2O$ (4.5 g) was transferred into a beaker containing H_4EDTA (3.0 g) in water (10 mL). The mixture was heated under stirring (30 min, 60 °C) until the crystalline HLnEDTA(aq) formed. It was then cooled, and potassium hydroxide (2.1 g) dissolved in water (10 mL) was added dropwise until a clear solution was obtained, pH 12.8. About fivefold excess of ethanol was then added, until the solution became turbid. Mother liquid was left standing until the majority of the salt crystallized (about 10 min). The precipitate was filtered, washed twice with ethanol (96% and 100%, respectively), and air-dried; yield about 40%. From the filtrate a second crop can be collected later. The complexes decompose above 310 °C. Aqueous solutions of these salts are alkaline, implying partial hydrolysis of the complex anion.

Analyses. The compounds were analyzed for C, H, N, K, Ln, EDTA, and peroxides. The analyses are in good agreement with the proposed formulas. E.g., Anal. Calcd for $K_3La(O_2)EDTA \cdot 6H_2O$: C, 17.6; H, 3.5; N, 4.1; K, 17.1; La, 20.3; O_2^{2-}, 4.7; EDTA, 42.1. Found: C, 17.4; H, 3.5; N, 4.0; K, 17.8; La, 20.2; O_2^{2-}, 4.8; EDTA, 42.1.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 457, in the region of 5000–400 cm^{-1}, using Nujol mulls. Powder photographs were recorded on a GE XRD-5, equipped with a scintillation counter, using Cu Kα radiation. Conductivity was measured in water in the concentration range 10^{-2}–10^{-4} M by using a 1000-Hz conductivity bridge. Proton NMR spectra were recorded at room temperature in D_2O by using a Hitachi Perkin-Elmer Model R20B instrument.

Results

Three series of complexes listed in Table I were prepared from aqueous solutions at controlled pH. The crystalline peroxo–EDTA–lanthanide salts represent the first stable rare-earth peroxo derivatives reported in the literature.

It has been observed that hydrogen peroxide does not bind firmly to lanthanide ions in acid solutions containing EDTA, where the species $Ln(EDTA)^-$(aq) is present. When the pH is raised to about 6–7, the reaction with hydrogen peroxide results in formation of salts of the formula KLnEDTA·

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Table I. Isomorphous Series of Complexes, Characterized by X-ray Powder Photographs (Cu Kα radiation)

	d, Å	approx I/I_0		d, Å	approx I/I_0		d, Å	approx I/I_0
			$KLn(EDTA)\cdot xH_2O_2\cdot yH_2O$					
$x = 0.5, y = 4$, Ln(III) = Y	9.83	>100	$x = 0.5, y = 6$, Ln(III) = Eu, Gd	9.51	52 (Eu)	$x = 2, y = 5$, Ln(III) = La, Nd	9.41	10 (La)
	5.04	41		8.59	43		8.59	100
	3.38	33		7.50	100		7.53	31
	2.14	33		3.11	61		3.11	82
				3.07	85		3.00	48
			$K_3Ln(O_2)EDTA\cdot xH_2O_2\cdot yH_2O$					
$x = 0, y = 3$, Ln(III) = Y	12.81	27	$x = 1, y = 5$, Ln(III) = Eu, Gd	11.71	100 (Eu)	$x = 0, y = 6$, Ln(III) = La, Nd	10.05	100 (La)
	11.95	100		8.43	74		9.03	85
	6.22	19		4.48	40		3.71	19
	3.00	14		3.12	40		2.99	44
			$K_2Ln(OH)(EDTA)\cdot 4H_2O$					
			Ln(III) = Y, La, Eu, Gd	11.12	100 (La)			
				5.51	19			

$xH_2O_2\cdot yH_2O$, which gradually decompose on heating and lose all peroxide by heating in vacuo at 100 °C. Isomorphism has been found for the pairs with the same number of peroxo groups and water molecules. The molar conductivity in water for these complexes amounted to 90–100 Ω^{-1} cm^2, in a range expected for a 1/1 electrolyte. For Ln = La, Nd complexes two different kinds of peroxides were observed. The first mole of oxygen is lost in vacuo over phosphorus pentoxide at room temperature and the second is removed with water in vacuo on prolonged heating at 100 °C. On standing at room temperature in a closed container, these complexes are losing some oxygen, but their powder pattern remains unchanged for weeks. The gradual loss of peroxo oxygen and water on heating in vacuo indicates the presence of loosely bound peroxides, or peroxohydrates.

Peroxo–EDTA complexes formed in alkaline solutions, $K_3Ln(O_2)EDTA\cdot yH_2O$ (y = 3 for Ln = Y; y = 6 for Ln = La, Nd) and $K_3Ln(O_2)EDTA(H_2O_2)\cdot 5H_2O$ (Ln = Eu, Gd), retain one peroxo group after prolonged heating in vacuo over P_2O_5 at 140 °C. This behavior is a strong indication that one peroxo group is firmly bound and coordinated to the lanthanide ion. Complexes of europium and gadolinium, which contain metal/peroxo ratios of 1/2, promptly lose 1 mol of hydrogen peroxide and retain 1 mol of the peroxo group. Isomorphous pairs are found, dependent upon the composition, as shown in Table I. Some samples of these complexes that were kept in closed containers at room temperature for more than 1 year did not lose peroxo oxygen and showed the original X-ray powder pattern. Some of the water molecules are lost on drying, one or two are retained, and the dry substances become hygroscopic. Aqueous solutions of these salts show molar conductivity between 400 and 500 Ω^{-1} cm^2, implying the presence of 3/1 electrolytes, as expected according to the formula. The aqueous solutions are alkaline due to the partial hydrolysis of the complex ion, which, however, does not seem to interfere with conductivity measurements in the concentration range 10^{-2}–10^{-4} M.

The infrared spectra of all EDTA derivatives are complex, and the spectra of peroxo–EDTA compounds are crowded with sharp, well-resolved bands, originating in EDTA vibrations. However, in spite of the rich spectrum, it is possible to detect some characteristic features. First of all, there is the strong, broad band with a maximum at 1600 cm^{-1}, comprising CO stretchings, which indicates the presence of coordinated carboxylato groups. The absorption is broad due to additional OH deformation modes which are expected here from the water molecules present. In the region between 800 and 900 cm^{-1}, where peroxo group stretchings are expected, reliable assignments are impossible without comparison with spectra of analogous complexes which do not contain peroxides. For this reason we have prepared the hydroxo–EDTA series of complexes, described later. Comparison of the spectra shows that an additional band appears for the peroxo–EDTA salts at 825 cm^{-1} for lanthanum, neodymium, europium, and gadolinium and at 840 cm^{-1} for the yttrium compound. This band indicates the presence of a coordinated peroxo group, originating in the O–O stretching mode.[12] We have previously successfully used such infrared evidence in predicting the structures of complexes which have later been confirmed by X-ray analysis.[5a,c,13,14] It is therefore worthwhile to look more carefully at these data. Spectral comparisons should be ideally carried out for isostructural ligand fields of the same symmetry; however, this is not possible here, and we can only use the best evidence available. Figures 1 and 2 show the representative infrared spectra in the region 1100–700 cm^{-1} and illustrate the case much better than a lengthy description or list of frequencies. Figure 1a shows the spectrum of K_2Y-

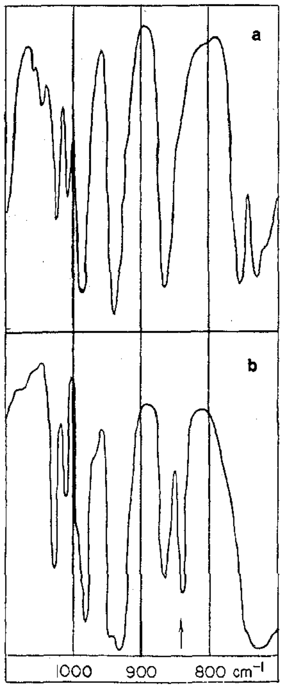

Figure 1. Infrared spectra of (a) $K_2[Y(OH)EDTA]\cdot 4H_2O$ and (b) $K_3[Y(O_2)EDTA]\cdot 3H_2O$, where the arrow indicates peroxo band at 840 cm^{-1}.

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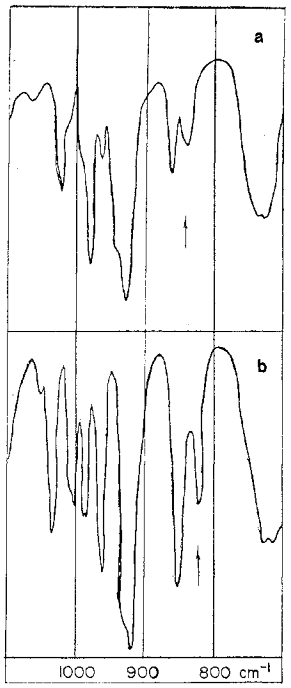

Figure 2. Infrared spectra of (a) $K_3[Y(O_2)EDTA]\cdot 3H_2O$ after heating, where the arrow indicates peroxo band at 840 cm^{-1}, and (b) $K_3[La(O_2)EDTA]\cdot 6H_2O$, where the arrow indicates peroxo band at 825 cm^{-1}.

$(OH)EDTA\cdot 4H_2O$, which is practically identical with the spectra of other derivatives in this isomorphous series, where Ln = La, Eu, and Gd. In Figure 1b the arrow indicates an additional band, found in the yttrium peroxo complex at 840 cm^{-1}, which is assigned to the coordinated peroxo group stretching. Figure 2a shows the infrared spectrum of the same compound after having been heated in vacuo (10^{-3} mmHg) at 140 °C for 4 h. The substance has, according to peroxide analysis, lost about 60% of the peroxo content after this prolonged heating in vacuo. The loss is clearly reflected in the diminished intensity of the 840-cm^{-1} band, and this simple experiment illustrates clearly the sensitivity of this absorption to the amount of peroxide present. Figure 2b shows the spectrum of the $K_3La(O_2)EDTA\cdot 6H_2O$ complex, where the peroxo stretching band appears at 825 cm^{-1}, the same frequency as observed for other complexes in this series, where Ln = Nd, Eu, and Gd. In comparison to the yttrium spectrum shown in Figure 1b, the peroxo stretching absorption appears at a 15 cm^{-1} lower frequency. We consider the mass sensitivity of this band as strong evidence in support of our assignment.

On comparison with the infrared spectra of hydroxo–EDTA lanthanide complexes we could not single out decisively any other vibrational bands expected from a coordinated peroxo ligand.[12] They may well be obscured by strong EDTA absorption in the crowded range between 700 and 450 cm^{-1}. Some shoulders may be detected, but without ^{18}O isotopic shift studies the discussion of infrared spectra in this region would consist of pure speculation.

The hydroxo–EDTA complexes $K_2Ln(OH)EDTA\cdot 4H_2O$, Ln = Y, La, Nd, Eu, and Gd, were actually prepared to study their spectra in comparison with spectra of peroxo derivatives. They were prepared from alkaline solutions under conditions similar to those for the peroxo–EDTA salts. These complexes are very soluble in water, and their aqueous solutions are alkaline. The previously known $KLn(EDTA)\cdot xH_2O$ salts are less soluble in water, and their aqueous solutions are acidic, containing the $Ln(EDTA)^-(aq)$ ion,[15,16] which was characterized in the solid state.[17] The hydroxo–EDTA complexes seem to be isomorphous, showing one prominent strong reflection in powder photographs. (See Table I.) The crystals which sometimes grow large seem to have cubic symmetry. Molar conductivity of these salts in aqueous solutions was found to be in the range between 250 and 350 Ω^{-1} cm^2, approximately expected and somewhat high for 2/1 electrolytes. Partial hydrolysis of the complex anion is probably responsible for these values.

Proton NMR spectra of peroxo–EDTA and hydroxo–EDTA complexes of the same lanthanide ion, studied in D_2O solutions, show different resonance patterns. Sharp singlets are observed for methylene (acetate) and ethylene (backbone) protons in spectra of diamagnetic lanthanum and yttrium peroxo–EDTA complexes. The methylene protons are split in the spectrum of $KY(OH)EDTA\cdot 4H_2O$. In all diamagnetic complexes, EDTA proton resonances are found on the high-field side of the HDO resonance, and there is no evidence for the presence of free EDTA ions. In the spectra of paramagnetic complexes, EDTA proton resonances are shifted strongly, as expected from these systems which act as internal shift reagents.

Discussion

Lanthanides do not form simple peroxo compounds.[1,2] In a way this behavior reflects the chemistry of rare earths: ionic character, but not strong enough to form ionic peroxides of the type alkaline-earth metals do. On the other hand, although typical A class Lewis acids, with a strong preference for oxygen donor ligands, the lanthanides are not like the rest of the d^0 early transition metal family, which forms a number of covalent peroxo anions and heteroligand complexes. The latter range from simple monoperoxohalo derivatives to large, bulky chelates, as for example peroxotitanium(IV) porphyrins.[18] Di- and triperoxo heteroligand complexes involving various bidentate oxygen or nitrogen donor ligands are known, including EDTA.[5,19]

$KLnEDTA\cdot xH_2O_2\cdot yH_2O$ salts, which were separated from solutions of pH 6–7, contain a mononegative complex ion. Their simultaneous oxygen release and water release suggest that a strong Ln–peroxo bond is not present. The $LaEDTA^-(aq)$ ion existing in weakly acid and neutral solutions of lanthanides with EDTA does not seem to bind firmly to peroxo ligands, yet some interaction with hydrogen peroxide does occur. The crystalline complexes obtained are more stable than previously reported hydroxoperoxo solids,[1,2] and their aqueous solutions show molar conductivity corresponding well with the presence of 1/1 electrolytes. The challenging question is of course: Where are the protons? They may be located on carboxylato or hydroperoxo groups, involving bridging hydrogen peroxide. Simple H_2O_2 adducts would probably not give the values of molar conductivity observed. Ionic peroxides are known for their ability to form well-crystallized hydrates and H_2O_2 adducts. Strong hydrogen bonding and the complexity of the EDTA infrared spectrum prevent any reliable speculation based on spectral evidence.

$K_3Ln(O_2)EDTA\cdot xH_2O_2\cdot yH_2O$ complexes, obtained from alkaline solutions, have distinctly different properties from complexes described above. One peroxo ion seems to be stabilized in the coordination sphere of the metal ion, and the monoperoxo–EDTA–lanthanide moiety survives prolonged heating in vacuo at 140 °C. On standing at room temperature

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the substances are stable for years. Infrared spectra of this series of complexes show the characteristic bands at 840 and 825 cm^{-1} for yttrium and other lanthanide complexes, respectively, as illustrated in Figures 1 and 2. The coordinated peroxo group can be considered as a local C_{2v} entity, and, with the absence of strong coupling assumed, three infrared-active modes are expected (2 A_1 + B_2). The corresponding frequencies have been reported for a variety of peroxo complexes[12] in the vicinity of 880 (O_2^{2-} stretching), 600, and 500 cm^{-1}. In EDTA complexes these regions are unfortunately crowded by EDTA bands, shifted to various degrees, depending upon the symmetry and environment of EDTA ligand. To obtain reliable information, we compare the spectra of related complexes available. The discussion of spectral evidence is based on the following: (1) comparison between spectra of the $K_2Ln(OH)EDTA$ and $K_3Ln(O_2)EDTA$ series, (2) comparison within the $K_3Ln(O_2)EDTA$ series itself, where Ln = Y, La, Nd, Eu, and Gd, and finally (3) comparison with the spectra of two related but nonisostructural complexes reported previously, $K_2Ti(O_2)EDTAH_2O$[19] and $K_3M(O_2)_3EDTA$ (M = Nb, Ta), along with those of some other heteroligand niobium and tantalum complexes.[5] In the first place, comparison of the spectra of analogous hydroxo– and peroxo–EDTA lanthanides reveals one additional band in the peroxo series, which is assigned to the peroxo stretching mode, expected at the observed frequency. The mass sensitivity of this band implies a complex nature of this absorption and coupling of peroxo stretching mode with a M–O vibration. Analogous metal sensitivity of peroxo stretching has been observed before for several isomorphous niobium and tantalum di- and triperoxo heteroligand complexes,[5] with characteristic doublets occurring between 870 and 840 cm^{-1}. These have been found invariably at a 10–20 cm^{-1} higher frequency for niobium derivatives. Consequently, appearance of the peroxo stretching in yttrium complex at a 15 cm^{-1} higher frequency than in other lanthanide complexes is in agreement with previous findings and strongly supports the proposed assignment. Other lower frequency bands expected from a peroxo group are obscured by EDTA vibrations. Comparison of the spectra of the $K_3Ln(O_2)EDTA$ series with the spectrum of $K_2Ti(O_2)EDTAH_2O$ would suggest that some of the three proposed peroxo group bands, shown for the titanium complex in the 1100–650-cm^{-1} range,[19] may well belong to EDTA modes, and further spectral study should clarify the assignment for this monoperoxo–EDTA titanium compound. The spectra of $K_3[M(O_2)_3EDTA]$, M = Nb, Ta, complexes are crowded in this region as usual, and the assignment of peroxo stretchings has been proposed by analogy with previous simpler peroxo heteroligand complexes of niobium and tantalum.

Infrared spectra of $K[Ln(EDTA)]\cdot nH_2O_2\cdot mH_2O$ complexes differ from the spectra of $K_3[Ln(O_2)EDTA]$ series. The pattern and intensity of EDTA bands are not the same, and frequencies are shifted too. Dissimilarity is most pronounced below 800 cm^{-1}. A shoulder appears around 820 cm^{-1}, which cannot be well resolved. This difference in spectral features reflects different symmetry of coordinated ligands in a different coordination sphere, but it is not possible to deduce from spectra any reliable assignment nor single out a particular additional band on comparison with spectra of related complexes.

These complexes are of interest from a structural point of view as well. Many years ago Hoard et al.[17] demonstrated the existence of 9-coordinated $LaEDTA(H_2O)_3^-$ ion and 10-coordinated $HLnEDTA(H_2O)_4$ acid in the solid state. Thermodynamics of the change in the number of coordinated water molecules was discussed in view of entropy increase upon decrease of the number of coordinated water molecules, concurring with a drop in standard enthalpy, due to the M–OH_2 bond breakage. In comparison to these two complex ions, $La(O_2)EDTA^{3-}$ anion is expected to have coordination number 8 or more, depending, among other factors, upon the enthalpy increase due to the lanthanide–peroxo bond formation. An extension of these thoughts leads to the series $KLn(OH)EDTA\cdot 4H_2O$. A long time ago[15,20] compounds of the composition $M^ILnEDTA\cdot xH_2O$ were prepared from acid solutions that contain the $Ln(EDTA)^-$(aq) anion. When the pH is raised, a proton obviously is removed from a coordinated water molecule and the anion $Ln(OH)EDTA^{2-}$(aq) exists in alkaline solutions. The interesting question is again: How does the deprotonation of the complex anion affect its structure, frozen in the solid state? The following trend may well be followed, with the negative charge increase causing the shrinking of the primary coordination sphere, as observed for the two species by Hoard et al.[17]

complex	coord no.
$HLa(EDTA)(H_2O)_4$	10
$La(EDTA)(H_2O)_3^-$	9
$La(OH)EDTA(H_2O)^{2-}$	8 (?)

Several proton NMR studies of transition-metal EDTA complexes were reported,[21] some for lanthanide complexes.[22–24] The resonance pattern for methylene (acetate) and ethylene (backbone) protons has been found indicative of the lifetime of M–O and M–N bonds, as well as of the symmetry environment of coordinated EDTA. Line-broadening techniques were used to determine ligand exchange and evaluate stability constants,[23] and the europium complex has been used as a model for europium shift studies.[8] Our observations of a different resonance pattern occurring for peroxo–EDTA and hydroxo–EDTA complexes of the same metal ion are interesting. They indicate a different symmetry environment of the protons, which may occur for various reasons (change in symmetry of coordination sphere, different lifetime of metal–ligand bonds, the presence of more than one isomer for one of these low-symmetry high-coordination-number polyhedra). More elaborate studies are necessary to explain these spectra and to elucidate the environment of the ligands in the coordination sphere, including the temperature-dependent proton NMR. Combination of the latter with ^{13}C, ^{14}N, ^{18}O, and metal ion NMR would be very interesting, and we plan to carry out these studies.

Existence of stable heteroligand peroxo–EDTA complexes of lanthanides confirms that, apart from the well-known differences between rare earths and early transition metals, there is a part of chemistry which demonstrates some remarkable similarity between these metal ions.

Registry No. KY(EDTA), 12558-70-2; KEu(EDTA), 33727-44-5; KGd(EDTA), 74128-00-0; KLa(EDTA), 54516-09-5; KNd(EDTA), 74128-01-1; $K_3Y(O_2)EDTA$, 74143-47-8; $K_3Eu(O_2)EDTA$, 74143-48-9; $K_3Gd(O_2)EDTA$, 74143-49-0; $K_3La(O_2)EDTA$, 74143-50-3; $K_3Nd(O_2)EDTA$, 74143-51-4; $K_2Y(OH)EDTA$, 74128-02-2; $K_2La(OH)EDTA$, 74128-03-3; $K_2Eu(OH)EDTA$, 74128-04-4; $K_2Gd(OH)EDTA$, 74128-05-5; $K_2Nd(OH)EDTA$, 74128-06-6.

Supplementary Material Available: Analytical procedures and analyses (percent) of all the compounds for carbon, hydrogen, nitrogen, lanthanide, potassium, peroxide, and EDTA (2 pages). Ordering information is given on any current masthead page.

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