coordinated via the oxygen atoms.[36]

At present, a number of iron complexes with quinone-like ligands are known. *o*-Semiquinone ligands are apparently stabilized when the *o*-semiquinone chelates to the iron(III) ion. Thus, the reaction of an *o*-quinone with $Fe(CO)_5$ gives a complex which we have characterized as a tris(*o*-semiquinone) complex of high-spin iron(III).[37] The reaction of Fe^{II}(salen) with an *o*-quinone gives an Fe^{III}(salen)(*o*-semiquinone) complex,[36] in which the salen ligand folds back to allow chelation of the *o*-semiquinone ligand.

The preparation of a similar complex with a semiquinone ligand coordinated to an Fe^{III}(TPP) moiety was not found to be possible. Repeated attempts to prepare such a complex by oxidative addition of Fe^{II}(TPP) with 9,10-phenanthrenequinone, 1,2-naphthoquinone, and 3,5-di-*tert*-butyl-*o*-benzoquinone in several hydrocarbon solvents did not result in formation of an Fe^{III}(TPP)(*o*-semiquinone) complex, because of the inability of the TPP ligand to fold back and permit chelation of the semiquinone to the iron. Finally, the reaction of a *p*-quinone with either Fe^{II}(salen) or Fe^{II}(TPP) does not yield a semiquinone complex, regardless of the stoichiometry of reactants. Two iron(II) complexes are oxidized with the concomitant two-electron reduction of the *p*-quinone to yield a binuclear ferric complex with a hydroquinone dianion as a bridge.

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Registry No. $[Fe(TPP)]_2$(DuQ), 73367-26-7; $[Fe(TPP)]_2$Q, 73367-27-8; $[Fe(TPP)]_2$(BrQ), 73367-28-9; $[Fe(TPP)]_2$(ClQ), 73367-29-0; $[Fe(TPP)]_2$(FQ), 73367-30-3; $[Fe(TPP)]_2$(DDQ), 73384-24-4; $[Fe(TPP)]_2$(Cl_4cat), 73367-31-4; $[Fe(TPP)]_2$(Br_4cat), 73367-32-5; Fe^{II}TPP, 16591-56-3; DuQ, 527-17-3; Q, 106-51-4; BrQ, 488-48-2; ClQ, 118-75-2; FQ, 527-21-9; DDQ, 84-58-2; Cl_4cat, 2435-53-2; Br_4cat, 2435-54-3.

Supplementary Material Available: Tables V–XI (experimental and calculated magnetic susceptibility data for the compounds studied) (7 pages). Ordering information is given on any current masthead page.

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Complexation of Lanthanides by Pyruvate

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Complexation of lanthanide cations by pyruvate was studied by titration calorimetry and ^{1}H NMR. From the relative intensities of the NMR peaks and the net stability constants, estimates were obtained for the stability constants for formation of the lanthanide pyruvate species when the pyruvate is in the keto, diol, and dimer forms. Estimates are also reported for the enthalpies and entropies of complexation of these various species. Both the thermodynamic and ^{1}H NMR data are consistent with binding of lanthanides only by carboxylate in the keto pyruvate complexes. However, in the diol complexes, chelation occurs via the α-hydroxy and the carboxylate groups.

Introduction

Complexation studies in aqueous solution of trivalent lanthanide ions with monocarboxylate and α-substituted monocarboxylate ligands have been reported by a number of laboratories.[1] Of the α-substituted ligands, amino and thio groups do not seem to be involved in the complexation while α-hydroxy ligands form chelates.[2] A report of complexation of Eu(III) by pyruvate assumed interaction of the keto form of pyruvate although Leussing has reported that keto, diol (hydrated enol), and dimer species of pyruvate are involved in the complexation of Zn(II).[3]

In this paper we report our measurements of the thermodynamic parameters of complexation of Ln(III) ions and pyruvate by an entropy calorimetric titration procedure. We also report ^{1}H NMR studies which provide information on the relative concentrations of the lanthanide complexes formed with the keto, diol, and dimer pyruvate species (Figure 1).

Experimental Section

Solutions for Calorimetry. Stock solutions of the lanthanide perchlorates were prepared as described previously.[4] Working solutions of $Ln(ClO_4)_3$ were prepared by diluting the stock solutions so that the final metal ion concentrations were approximately 0.025 M. The ionic strength of all the solutions was adjusted to 2.0 M with $NaClO_4$, and the pH of the solutions was adjusted to a value between 2.0 and 2.2.

An aqueous stock solution of pyruvic acid was prepared from 25 g of reagent grade pyruvic acid (J.T. Baker Chemical Co.) and standardized against standard sodium hydroxide. The working solution of pyruvate was a buffer solution prepared by half neutralizing the pyruvic acid with an appropriate amount of sodium hydroxide. The ionic strength was maintained at 2.0 M by addition of $NaClO_4$. The final solution was 0.50 M in pyruvic acid, 0.25 M in NaOH, and 1.75 M in $NaClO_4$ at a pH of 2.2.

Solutions for NMR. Samples for NMR measurements were prepared by using solvent D_2O from Mallinckrodt Chemical Works with a minimum isotopic purity of 99.8%. The internal reference standard used in all samples was sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) from Merck Co.

The sodium pyruvate samples were prepared by dissolving a weighed amount of reagent grade sodium pyruvate in D_2O. Solutions were adjusted to a pD range of 0–6.

Lanthanum and lutetium perchlorate solutions in D_2O were prepared by taking appropriate aliquots of the stock solutions to dryness several times in D_2O. Sodium pyruvate was added to obtain a metal to ligand ratio of 6:1 at which most of the pyruvate is bound in the 1:1 complex. Lanthanum pyruvate solutions were prepared at pD 2 and 4 while lutetium pyruvate was prepared at pD 2 only due to its lower solubility at higher pD values.

Calorimetry. The calorimeter used in this study has been described in detail.[4] The general procedure used for calorimetric measurements in this study has been described by other workers from this laboratory.[4,5] The heats of complexation were obtained for all the lan-

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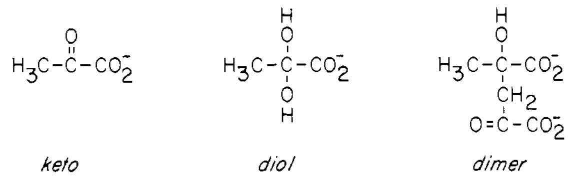

Figure 1. Species present in pyruvate solutions of metal ions.

Table I

Entropy Titration Data for the Neodymium-Pyruvate System (I = 2.0 M ($NaClO_4$); T = 25.0 °C)

titer vol, mL	$-Q_i$, mcal	10^3[L], M	10^3[M], M	10^3[H], M
0.12	−0.34	0.636	24.470	6.710
0.24	−0.59	1.259	23.970	7.011
0.36	−0.86	1.874	23.500	7.283
0.48	−0.46	2.479	23.040	7.530
0.75	1.85	3.818	22.090	8.010
1.03	3.31	5.177	21.180	8.420
1.30	7.38	6.468	20.380	8.750
1.57	11.89	7.743	19.640	9.028
1.85	16.22	9.051	18.920	9.273
2.15	22.09	10.440	18.200	9.496
2.46	27.10	11.860	17.510	9.690
2.76	34.13	13.230	16.890	9.849
3.06	40.22	14.590	16.310	9.986
3.37	46.33	15.980	15.740	10.100
3.67	53.45	17.320	15.230	10.200
3.98	59.85	18.700	14.730	10.290
4.29	66.55	20.060	14.260	10.370

Experimental Conditions

metal solution	titer
[Nd] = 0.0250 M	[total ligand] = 0.5034 M
pH 2.1955	pH 2.2003

Computed Thermodynamic Parameters
β = 2.91 ΔH = −1.13 kcal/mol

Table II

Calorimetric Data for the Heat of Protonation (I = 2.0 M ($NaClO_4$); T = 25.0 °C)

titer vol, mL	Q_i, mcal	$[(HL) - (HL)_i] V_T$, mol
0.36	38.6	3.37×10^{-2}
0.72	94.4	6.74×10^{-2}
1.08	159.4	1.01×10^{-1}
1.43	227.7	1.34×10^{-1}
1.79	300.3	1.67×10^{-1}
2.14	374.7	1.99×10^{-1}
2.50	446.6	2.33×10^{-1}
2.86	519.6	2.66×10^{-1}
3.21	597.5	2.98×10^{-1}
3.57	673.9	3.31×10^{-1}
3.92	748.5	3.64×10^{-1}
4.28	824.7	3.96×10^{-1}
4.63	900.1	4.28×10^{-1}
4.99	974.5	4.61×10^{-1}

Experimental Conditions

sodium pyruvate solution	perchloric acid solution
concentration = 0.125 M	concentration = 0.101 M
initial volume = 50.0 mL	initial [H] = 1.01×10^{-1} M
initial [H] = 2.00×10^{-6} M	

Thermodynamic Protonation Constants
β_p = 98.0 ΔH_p = 2.03 kcal/mol

Table III. Thermodynamic Parameters of Ln(III)-Pyruvate Complexation (I = 2.0 M ($NaClO_4$); T = 25.0 °C; pH 2.2)

lanthanide	β_1 [a]	ΔG_1, [b] kcal/mol	ΔH_1, [b] kcal/mol	ΔS_1, [c] cal/(deg mol)
La	10.0	−1.36	−0.89	1.6
Ce	39.2	−2.17	−1.07	3.7
Pr	52.0	−2.34	−1.13	4.1
Nd	29.1	−2.00	−1.13	2.9
Sm	33.5	−2.08	−1.16	3.1
Eu	75.0	−2.56	−1.17	4.7
Gd	46.8	−2.28	−1.18	3.7
Tb	15.6	−1.63	−1.00	2.1
Dy	18.6	−1.73	−1.08	2.2
Ho	21.7	−1.82	−1.01	2.7
Er	52.3	−2.34	−1.12	4.1
Tm	78.0	−2.58	−1.11	4.9
Yb	35.9	−2.12	−1.21	3.1
Lu	67.9	−2.50	−0.96	5.2

[a] ±10%. [b] ±0.05. [c] ±0.2.

thanides by titrating 50.0 mL of each metal solution with increments of buffered ligand solution. Corrections for the heat of dilution were obtained by titrating a 50.00-mL sample of 2.0 M sodium perchlorate (pH 2.1) with the pyruvate buffer solution. The heat of dilution was exothermic and significant since a 0.50-mL addition of buffer produced approximately 8 mcal of heat.

The heat of protonation of the pyruvate anion was determined by titration of a 50.0-mL solution of 0.125 M NaP (I = 2.1 M) with 0.10 M $HClO_4$ (I = 2.0 M). The heat of dilution from a titration of 2.0 M $NaClO_4$ with 0.10 M $HClO_4$ was found to be negligible compared to the heat of protonation. An overall pK_a value of 2.1 has been reported for pyruvic acid in 1 M NaCl[6] and 2.4 in 3 M $NaClO_4$[7] while our measurements gave 2.0 for 2.0 M $NaClO_4$. We use this latter value in our calculations (pK_a = 2.4 would decrease our calculated values of β by 10%).

^{1}H NMR Measurements. The NMR measurements were made on Bruker 90-MHz and Bruker 270-MHz spectrometers using a pulsed Fourier transform technique. Chemical shifts are reported in ppm relative to the signal for the three equivalent methyl groups of the DSS internal standard. Temperature studies in a range from 5 to 85 °C were carried out by using a temperature controller with a thermocouple placed just below the sample.

Results

The usual pH titration method to obtain stability constants cannot be employed for relatively strong acid ligands (pK_a < 3). However, in this case we expected the stability constants and the enthalpies of complexations to fall within the range considered most effective for the entropy titration technique[8] ($-1 < \log \beta_1 < 2$; $|\Delta H_1| > 1$ kcal/mol) whereby β and ΔH are determined simultaneously. A typical set of data of such a titration are presented in Table I while Table II gives the calorimetric data for the heat of protonation. For most lanthanides, two or more titrations were performed and the data analyzed as described previously.[4] The K_a and ΔH_a protonation values were used as constants in the calculations which gave no evidence for formation of higher complexes such as LaP_2. The calculated (averaged) thermodynamic parameters are listed in Table III.

For validation by independent measurement of the results of the entropy titration method, the stability constants for Eu(III) and pyruvate at 2.0 M ($NaClO_4$) ionic strength were determined by a radiotracer solvent extraction procedure.[9] The β_1 value of 79 ± 14 (95% confidence level) agreed well with the values of 75 ± 8 from entropy titration.

The observed peaks and their relative intensities of the methyl resonances of the ^{1}H NMR spectra of the sodium, lanthanum, praseodymium, and lutetium pyruvate solutions are listed in Table IV. All peaks were narrow, except those

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Table IV. Peaks and Relative Intensities in ^1H NMR Spectra (T = 25 °C)

sample	pD	peaks[a] keto	diol	dimer	lactone
NaP	0	2.47 (42%)	1.57 (58%)		
NaP	2	2.41 (59%)	1.58 (41%)		
NaP	3	2.39 (86%)	1.55 (14%)		
NaP	4	2.37 (94%)	1.49 (6%)		
NaP	6	2.37 (96%)	1.49 (4%)		
LaP	2	2.49 (66%)	1.59 (20%)	1.53 (22%)	
PrP	2	2.32 (61%)	3.11 (25%)	2.56 (14%)	
LuP	2	2.51 (6%)	1.59 (6%)	1.52 (64%)	1.67, 1.79, 1.94 (24%)

[a] Numbers given are in ppm relative to DSS.

of PrP which were somewhat broader, indicating rapid exchange between the complexes and free ligand of each particular pyruvate species. By contrast, the presence of separate peaks means that exchange between the various pyruvate species must be slow on an NMR time scale. A solution of 0.53 M La(III), 0.03 M Cr(III), and 0.23 M pyruvate at pH 3 was also run. The peaks showed broadening but were not shifted from those observed in the same solution in the absence of Cr(III). The positions and assignments of the peaks agreed with Leussing's earlier study.[3] Table V gives the results of the temperature studies.

Discussion

A previous ^1H NMR study[3] of pyruvate solutions at various values of pH has provided estimates of $pK_a^{keto} = 2.0$ and $pK_a^{diol} = 3.6$ in 1 M solutions. From the data in Table IV we estimate $pK_a^{keto} = 2.0$ and $pK_a^{diol} = 3.4$ for our solutions of about the same concentrations. Pyruvic acid also dimerizes in aqueous solution although the rate is slow for pH ≤5 and in the absence of metal ions. The values reported for the acid dimer are $pK_{a1}^{dm} = 1.73$ and $pK_{a2}^{dm} = 3.72$ in 1 M NaCl.[6] It would seem that pK_{a1}^{dm} describes the acidity of the carboxylate associated an α-keto group while pK_{a2}^{dm} describes the acidity of the carboxylate bound to an α-hydroxy group.

The thermodynamic parameters in Table III relate to the formation of a combination of lanthanide complexes involving the keto, diol, and dimer forms of pyruvate. As such, they are useful to describe the net complexation. However, it is of some interest to estimate the thermodynamic parameters of the individual complexation reactions. The relative intensities of the ^1H NMR peaks of Table IV can be used to obtain such estimates of individual stability constants. A system of equations can be written which involves (a) three equations for the stability constants for the individual reactions of the keto (k), the diol (d), and the dimer (dm) species (i.e., i = k, d, or dm)

$$\beta_1^{i} = (LnP^{i})/(Ln)(P^{i}) \tag{1}$$

(b) two equations for the acid equilibria

$$K_a^{i} = (HP^{i})/(H)(P^{i}) \tag{2}$$

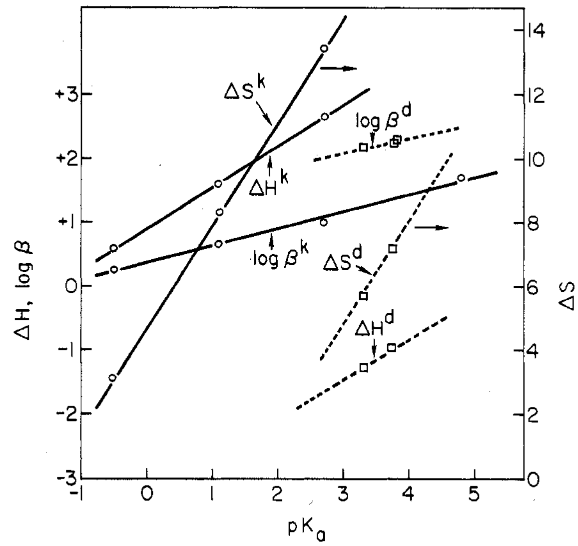

Figure 2. Relationship between log β, ΔH, and ΔS of complexation and ligand pK_a for monocarboxylates (solid lines) and α-hydroxy carboxylates (dashed lines).

(c) two mass balance equations for total lanthanide $(Ln)_T$ and total pyruvate $(P)_T$

$$(Ln)_T = (Ln) + \sum(LnP^{i}) \tag{3}$$

$$(P)_T = (P^k) + (P^d) + 2(P^{dm}) + (LnP^k) + 2(LnP^{dm}) \tag{4}$$

and (d) three equations for relationships within the pyruvate system as determined from the HP and NaP solution ^1H NMR spectra

$$(P^k) = 27.6(P^d) \tag{5a}$$

$$(P^{dm}) = 6.3(P^k)^2 \tag{5b}$$

$$(HP^k) = 0.72(HP^d) \tag{5c}$$

With these equations, the relative intensities of the ^1H NMR peaks and knowledge of $(Ln)_T$ and $(P)_T$ in the ^1H NMR experiments, we calculate for La(III)–pyruvate complexing: $\beta^k = 8$, $\beta^d = 59$, and $\beta^{dm} = 18$. In our thermodynamic measurements

$$\beta_T = \frac{(LaP^k) + (LaP^d) + 2(LaP^{dm})}{(Ln)[(P^k) + (P^d) + 2(P^{dm})]} \tag{6a}$$

$$\beta_T = \frac{\beta^k(P^k) + \beta^d(P^d) + 2\beta^{dm}(P^{dm})}{\sum(P^{i})} \tag{6b}$$

β^T is calculated with the estimated β^i values to be 11 compared to the experimental value of 10. These values of β^i suggest

Table V. Results of the NMR Temperature Study (pD 2.0)

sample	T, °C	peaks[a] keto	hydrate	dimer	lactone
LaP	10	2.49 (54.8%)	1.60 (31.0%)	1.53 (14.2%)	
LaP	20	2.48 (62.7%)	1.59 (24.0%)	1.52 (13.3%)	
LaP	25	2.49 (66.5%)	1.59 (20.0%)	1.53 (13.5%)	
LaP	35	2.48 (62.0%)	1.59 (14.0%)	1.53 (54.1%)	
LuP	10	2.50 (6.8%)	1.58 (22.8%)	1.51 (46.3%)	1.67, 1.78, 1.94 (24.1%)
LuP	15	2.48 (8.1%)	1.57 (22.7%)	1.50 (50.4%)	1.64, 1.76, 1.92 (18.8%)
LuP	25	2.51 (5.7%)	1.59 (5.7%)	1.52 (64.8%)	1.67, 1.79, 1.94 (23.8%)
LuP	35			1.53 (62.2%)	1.67, 1.79, 1.95 (37.8%)
LuP	50			1.54 (39.8%)	1.68, 1.79, 1.95 (60.2%)

[a] Numbers given are in ppm relative to DSS.

that the keto ligand acts as a monodentate carboxylate complexor whereas the diol acts as a chelator similar to lactate.[10] This interpretation is supported by the Pr(III) ^{1}H NMR data which shows a large paramagnetic shift for the complexed diol and a smaller one for the keto ligand. The shift for the dimer ligand is in between and, coupled with the calculated value of β^{dm}, would seem to reflect that the complexation is not restricted exclusively to either the α-keto or the α-hydroxy end of the dimer.

Linear relationships have been shown to exist for ΔG, ΔH, and ΔS of complexation as a function of ligand pK_a for series of related ligands where the metal–ligand interaction is predominantly electrostatic. Figure 2 shows plots of log β_1, ΔH_1, and ΔS_1 vs. pK_a for the series Ce(III) complexation by $CH_{3-n}Cl_nCO_2^-$ (n = 0–3).[11] Also included are the plots for Ce(III) complexation by glycolate[9] and mandelate.[12] From the pK_a values for the keto (2.0) and diol (3.4) pyruvate, we can estimate these values for the Ce(III) complexes: log β^k = 0.9, ΔH^k = +2.2 kcal/mol, ΔS^k = +11.1 cal/(deg mol); log β^d = 2.2, ΔH^d = −1.2 kcal/mol, ΔS^d = +6.2 cal/(deg mol). The dimer complex should have values between these. The ^{1}H NMR temperature data in Table V is not conclusive, but if we consider the intensity changes between 10 and 25 °C (above 25 °C it is likely that changes in the $2P^k = 2P^d = P^{dm}$ equilibria obscure the trends), ΔH^k would be endothermic, ΔH^d exothermic, and ΔH^{dm} almost zero. A surprising feature of these data is that ΔS_{exp}(CeP) is +3.7 cal/(deg mol) so no fractional combination of ΔS^k and ΔS^d values (all >6 cal/(deg mol)) can give a value <6 cal/(deg mol).

This dilemma is resolved upon realization that the reaction whereby ΔH^i was measured corresponded to reaction 7 since

$$\mathrm{Ln} + \mathrm{P^k} = \mathrm{LnP^i} \tag{7}$$

the pyruvate anion is >97% in the keto form in the absence of metal ions at pHs ~3–4. Therefore, for the diol reaction, the proper equation is

$$\mathrm{Ln} + \mathrm{P^k} + \mathrm{H_2O} = \mathrm{LnP^d} \tag{8}$$

Hydration is significant in the magnitude of the enthalpy and entropy terms but due to the "compensation effect" affects the free energy much less.[2,13,14] In other words, the extra enthalpy and entropy related to hydration roughly cancel so $\delta\Delta H \approx \delta T\Delta S$. Moreover, for one water molecule, $\Delta S \approx 8$–9 cal/(deg mol).[14] Therefore, to obtain ΔH and ΔS for the reaction Ln + P^k = LnP^k, we should subtract 9 cal/(deg mol) from the ΔS^α and 2.7 (0.3 × 9) kcal/mol from the ΔH^α. The "corrected" values are $\Delta H_c^{\,d}$ = −3.9 kcal/mol and $\Delta S_c^{\,d}$ = −2.8 cal/(deg mol).

If

$$\Delta G_T = f_k\Delta G_k + f_d\Delta G_d \tag{9}$$

($f_{dm}\Delta G_{dm}$ is a relatively small factor and would resemble roughly equal contributions to $f_k\Delta G_k$ and $f_d\Delta G_d$ so it can be neglected in a first approximation), for Ce(III) we obtain $f_k \approx 0.46$ and $f_h \approx 0.54$. Using these to estimate ΔH_T and ΔS_T in equations analogous to (9), we calculate $\Delta H_T \approx 1.1$ kcal/mol and $\Delta S_T \approx 3.6$ cal/(deg mol) which agree very well with the values for Ce(III) in Table III.

Summary

The thermodynamic and ^{1}H NMR data are consistent with formation of lanthanide–keto pyruvate complexes in which the lanthanide binds only to the carboxylate group. Lanthanide–diol pyruvate complexes also form involving chelation as in other α-hydroxy carboxylate ligands. Lanthanide–dimer pyruvate complexes are formed via coordination to the keto carboxylate in some instances and via chelation to the α-hydroxy carboxylate end in others. For La(III) and Ce(III) estimated values are

	β_T	β^k	β^d	β^{dm}
LaP	10	8	59	18
CeP	40	8	158	?

$\Delta H^k(\mathrm{CeP^k}) = +2.2$ kcal/mol $\Delta S^k(\mathrm{CeP^k}) = 11.1$ cal/(deg mol)
$\Delta H_c^{\,d}(\mathrm{CeP^d}) = -3.9$ kcal/mol $\Delta S_c^{\,d}(\mathrm{CeP^d}) = -2.8$ cal/(deg mol)

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Registry No. La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm, 7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3; pyruvic acid, 127-17-3.

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