Preparation of Some Lanthanoid Picrates and the Behavior of Their Water of Hydration[1)]

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Lanthanoid(III) picrates (Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, and Yb) were prepared from picric acid and the corresponding lanthanoid carbonates in good yields. Combustion analyses, ICP emission analyses, and UV spectrophotometry have shown that the light lanthanoid picrates, i.e. Ln=La-Gd, are all undecahydrates, while the heavy ones, Dy and Yb, are octahydrates. An examination by TG-DTA has revealed that these hydrates, being fairly stable in air at ambient temperature, are quite labile to give partially or completely dehydrated samples upon drying under vacuum, in a desiccator, and/or at elevated temperatures just above 30 °C.

Picrates have long been used in industry as initiating explosives and fuel additives.[2)] They have also been used in analyses, especially in the solvent extraction technique owing to the highly lipophilic nature of the picrate ion. Recently, the cation-binding abilities of neutral ligands like crown ethers have been conveniently evaluated by the extractability of aqueous metal picrates.[3)] For this purpose, alkali (Na-Cs),[4)] alkaline earth (Mg-Ba),[3,5)] and some heavy metal (Ag, Tl) picrates[3,6)] were synthesized and isolated. On the other hand, lanthanoid picrates have only been prepared in situ in solvent extraction experiments with some crown ethers;[7)] no practical method for preparing lanthanoid picrates has been published and their characterization has not been fully described. In this paper, we wish to report on a method for preparing some lanthanoid picrates and the characterization of their crystals.

Results and Discussion

Synthesis. The reaction of picric acid with metal hydroxide is a common route to obtain metal picrates, as in the case of alkali metal picrates.[4)] Since lanthanoid hydroxides are not commercially available and some heavy metal picrates have been prepared from the metal oxides,[3,6)] we first tried lanthanoid oxide. The reaction of picric acid with La oxide was carried out in hot water, but only the starting materials were recovered from the mixture.

Lanthanoid carbonates were then tried and gave satisfactory results regarding the preparation of La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, and Yb picrates. The reaction conditions were optimized in order to obtain the recommended procedure shown in the Experimental section. First examined were the effects of the molar ratio of picric acid to lanthanoid carbonate upon the product yield and purity. With Ce carbonate taken as an example, the picric acid/carbonate ratio (n) was changed from 1 to 9. Although no precipitation was obtained upon cooling when $n=1$, a yellow precipitate was formed at $n>3$. The yield generally increased with increasing n. However, as shown by spectrophotometric examination of dichloromethane extracts of the crystalline products, the use of excess picric acid, i.e. $n>6$, led to a significant contamination of the resulting picrate with picric acid, even after repeated recrystallizations from water. Therefore, $n<6$ should be used in order to obtain a pure sample free from picric acid in high yield.

The fresh lanthanoid picrate recrystallized from water gradually lost its weight (by ca. 10—18%) upon air-drying for 3—5 d at room temperature; after that period, practically no weight change (>1%) was observed during the next 85 d. The samples used in subsequent experiments were, therefore, air-dried for more than one week and stored in stoppered vials in the dark.

The lanthanoid picrates prepared as above were analyzed by means of an inductively coupled plasma (ICP) atomic emission analysis as well as by a combustion analysis. As shown in Table 1, the results from both analyses are in good agreement with the values calculated for the undecahydrates of light lanthanoid picrates (Ln=La-Gd) and for octahydrates of heavy ones (Dy, Yb). The UV spectra of their aqueous solutions also support this conclusion. As shown in Table 1, all picrates show almost identical molar extinction coefficients around 42000 $M^{-1} cm^{-1}$,[§] indicating that they contain the same numbers of water of hydration as determined by the elemental analyses.

The fact that the light and heavy lanthanoid picrates contain different numbers of water of hydration may be related to the well-documented *"gadolinium break"* observed for thermodynamic data of the lanthanoid series in aqueous solution, where a plot of such data as a function of ionic radius often exhibits a break somewhere in the middle of the lanthanoid series. This break is considered to reflect a discontinuous variation in the hydration structures of the lanthanoid ions.[8)]

[§] 1 M=1 mol dm^{-3}.

Table 1. Elemental Analyses and Some Properties of Lanthanoid Picrate Hydrates ($\mathrm{Ln(Pic)_3\cdot xH_2O}$)

Compound	Mol wt	Yield/%	Content/%[a]				Dp/°C[b]	Ep/°C[c]	ε_{max}/$M^{-1}cm^{-1}$[d]
			Ln	H	C	N			
$\mathrm{La(Pic)_3\cdot 11H_2O}$	1021.40	56	12.9	2.57	21.21	12.22	292	340	42100
			(13.6)	(2.76)	(21.17)	(12.34)			
$\mathrm{Ce(Pic)_3\cdot 11H_2O}$	1022.61	86	13.6	2.54	20.98	12.35	270	316	42200
			(13.7)	(2.76)	(21.14)	(12.33)			
$\mathrm{Pr(Pic)_3\cdot 11H_2O}$	1023.40	76	13.6	2.76	21.44	12.19	284	337	41600
			(13.8)	(2.76)	(21.13)	(12.32)			
$\mathrm{Nd(Pic)_3\cdot 11H_2O}$	1026.73	56	14.0	2.35	20.85	12.15	288	344	42100
			(14.1)	(2.75)	(21.06)	(12.28)			
$\mathrm{Sm(Pic)_3\cdot 11H_2O}$	1032.84	65	14.8	2.65	20.68	11.90	286	342	42100
			(14.6)	(2.73)	(20.93)	(12.21)			
$\mathrm{Eu(Pic)_3\cdot 11H_2O}$	1034.45	45	15.5	2.50	20.60	11.83	292	342	40900
			(14.7)	(2.73)	(20.90)	(12.19)			
$\mathrm{Gd(Pic)_3\cdot 11H_2O}$	1039.74	33	15.2	2.42	20.49	11.89	288	346	42100
			(15.1)	(2.71)	(20.79)	(12.12)			
$\mathrm{Dy(Pic)_3\cdot 8H_2O}$	990.95	69	16.5	2.13	21.73	12.71	285	350	42700
			(16.4)	(2.24)	(21.82)	(12.72)			
$\mathrm{Yb(Pic)_3\cdot 8H_2O}$	1001.49	42	17.4	2.13	21.59	12.51	260	348	43000
			(17.3)	(2.21)	(21.59)	(12.59)			

a) Determined by ICP for Ln and by combustion analysis for H, C, and N; calculated values (%) are shown in the parentheses. b) Decomposition point determined by DTA. c) Explosion point determined by DTA. d) Molar absorption coefficient at the absorption maximum (354 nm) in water.

Studies on the apparent molal volume and X-ray diffraction data of aqueous rare earth salt solutions suggest that the coordination number in the first solvation shell of a lanthanoid ion shifts from nine to eight between neodymium and terbium.[8f,g] The present change in the number of the water of hydration lies in the same line, although the coordination number in the crystalline state is not necessarily identical to that in an aqueous solution.

The Behavior of the Water of Hydration. Interestingly, the water in lanthanoid picrate hydrates was shown to be quite labile. Although the light lanthanoid picrates, La-Gd, do not change in weight (within ±1%) in open air, they gradually lose weight to reach ca. 85 % of the original weights when stored over SiO_2 in a desiccator for 3 d or more. Thus, SiO_2 removes 8—9 out of 11 water molecules, leaving a tri- or dihydrate. Vacuum-drying over P_2O_5 resulted in complete dehydration, as indicated by a 17—19% loss of the original weight which corresponds to a loss of 11 water molecules from each picrate of a light lanthanoid.

In order to further investigate the behavior of the water of hydration, samples of La picrate at different drying stages were subjected to thermal analyses. The thermogravimetry-differential thermal analysis (TG-DTA) curves obtained are shown in Fig. 1. For the air-dried sample (curves A), the first endothermic peak in the DTA curve starts just above room temperature (30 °C) and reaches a maximum at 50 °C. This causes a considerable loss of weight (cf. the TG curve A). The second weak endothermic peak appears near 90 °C with a smaller loss of weight. The weight loss at each peak roughly coincides with that observed upon drying over SiO_2 and P_2O_5 in vacuo, respectively. Further heating gives an exothermic peak at 292 °C, i.e. the decomposition point of La picrate, and finally results in an explosion at 340 °C.[§§]

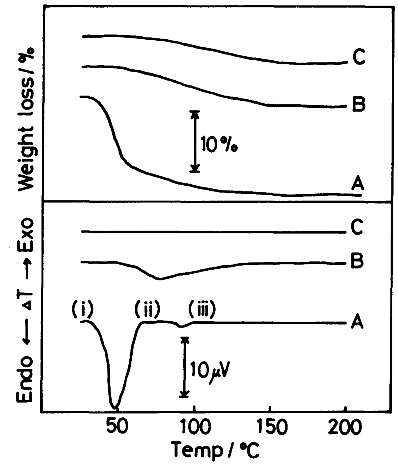

Fig. 1. TG-DTA curves for air-dried (A), SiO_2-dried (B), and P_2O_5-in vacuo dried (C) samples of La picrate; see Experimental for detailed conditions of measurement.

With the SiO_2-dried sample (curves B), only a broad peak around 75 °C appears in DTA curve B with a small decrease in the TG curve. The sample vacuum-dried over P_2O_5 did not show any evident peak in DTA curve C; TG curve C declined slightly, but this could be ascribed to the loss of a small amount of water reabsorbed before the DTA measurement since the vacuum-dried sample was highly hygroscopic.

Air-dried samples of Ce, Pr, and Nd picrate hydrates

[§§] Caution should be exercised in handling metal picrates, since they are shock- and heat-sensitive. Although most lanthanoid picrates did not explode below 300 °C, heating of sodium picrate at >250 °C resulted in an explosion which destroyed the thermocouple of the DTA apparatus.

also gave analogous TG-DTA curves with the first large endothermic peak at ca. 50 °C and a subsequent small peak at ca. 90 °C; Sm, Eu, and Gd picrates gave an additional endothermic peak around 140 °C. Dy and Yb picrate octahydrates exhibited similar TG-DTA curves with two endothermic peaks around 55 and 85 °C; however, the peak intensities were inverted. These observations support the idea that lanthanoid picrate hydrates possess at least two kinds of water; one is loosely bound and is released easily by mild drying over SiO_2 or by heating just above room temperature. The other is tightly bound and is removed by vacuum-drying over P_2O_5 or by heating up to 90—140 °C. This behavior of the water of hydration in lanthanoid picrates is in sharp contrast with that of alkali or alkaline earth picrate hydrates which do not lose water at such low temperatures as 30—50 °C. It has been reported that most mono- and divalent metal picrates show the first endothermic peak well above 100 °C,[9] which would correspond to the second peak in the lanthanoid picrate case.

The structural change of an air-dried La picrate caused by dehydration can be visualized by X-ray diffraction patterns. As can be seen in Fig. 2, the diffraction pattern of the air-dried sample (stage i in Fig. 1), indicates the presence of a well-defined crystal structure, while the sample obtained by rapid cooling just after the first endothermic peak (stage ii) yielded a more complicated diffraction pattern (which still maintained the original peaks at the same angles). This indicates that a certain phase change takes place between stages i and ii. Further heating up to 110 °C, i.e. to the end of the second endothermic peak (stage iii), leads to the disappearance of all sharp diffraction peaks (top trace in Fig. 2), indicating that the original crystal structure is totally broken by a complete loss of water. The samples dried over SiO_2 or P_2O_5 in vacuo also show no sharp X-ray diffraction patterns at all; these samples are all highly hygroscopic but do not regenerate the original undecahydrate upon standing in a moderately humid atmosphere at room temperature. Also observed was an apparent change in color of the crystalline lanthanoid picrates from yellow to deep orange or to red upon heating up to ca. 120 °C or upon drying in vacuo, which may again be accounted for in terms of the drastic structural change.

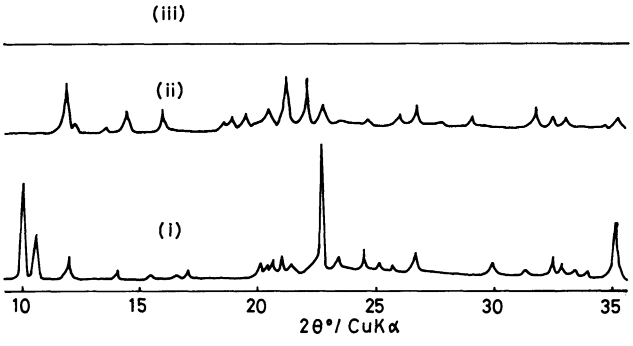

Fig. 2. X-Ray diffraction patterns of La picrate at different stages (i—iii) of the thermal analysis as shown in Fig. 1.

It may be summarized as follows: 1) the lanthanoid(III) picrates (Ln=La-Gd, Dy, Yb) are prepared in good yield by the reaction of picric acid with the corresponding carbonate in hot water, 2) the picrates prepared are undecahydrates for the light lanthanoids La-Gd and octahydrates for the heavy lanthanoids Dy and Yb, and 3) the water of hydration can be removed easily when stored over a desiccant under atmospheric or reduced pressure, to give partially or completely dehydrated samples, which suffer a phase change and turn highly hygroscopic. It is therefore recommended that the lanthanoid picrates recrystallized from water should merely be air-dried and be used as hydrates without further drying. The present method should be applicable to the synthesis of the rest of lanthanoid picrates, which are inferred to be octa- or undecahydrates.

Experimental

Materials. Commercially available picric acid and lanthanoid carbonates and oxides (G.R. or E.P. grade) were used without further purification. Deionized water was used throughout the study.

Instruments. It was first attempted to measure the melting and decomposition points in a capillary tube with a Yanaco hot-stage micro melting point apparatus. However, the obtained mps were the same (around 65 °C) for some light lanthanoid picrates, for which the release of the water of hydration must be responsible. Measurements on an open glass plate are also difficult due to an apparent carbonization of a sample above 230 °C. Decomposition and explosion points (dp and ep) were therefore determined from the extrapolated onsets of the exothermic peaks of DTA curves; these peaks accompanied a moderate and an extreme loss of weight in the TG curve, respectively.

TG-DTA curves were recorded on a Rigaku differential thermal balance model 8076 equipped with a platinel thermocouple; sample size: 5 mg picrate + 5 mg baked α-alumina; air-flow: 75 ml min^{-1} for air-dried samples and no flow for the samples dried over desiccants; scanning speed: 5 or 10 °C min^{-1}. Electronic spectra were obtained on a Shimadzu UV-365 spectrophotometer. Infrared spectra were recorded on a Jasco IR-810 instrument. X-Ray diffraction patterns were recorded on a Rigaku X-ray diffraction equipment. ICP analyses were performed on a Shimadzu GVM100P inductively coupled plasma atomic emission spectrometer. The ICP instrument was calibrated for each metal with standard solutions prepared by dissolving lanthanoid oxides which were baked at 900 °C for 2 h in hydrochloric acid or, in Ce oxide case, in a 1 : 1 mixture of sulfuric acid and concentrated hydrogen peroxide.

Synthesis. Lanthanum Picrate Undecahydrate. To picric acid (3.4 g, 15 mmol) dissolved in hot water (100 ml) was added portionwise La carbonate (trihydrate; 1.3 g, 2.5 mmol) with stirring on a water bath at 80—90 °C. The stirring was continued for an additional 10 min at that temperature. The hot mixture was filtrated and then cooled with ice. The crude La picrate, obtained as a yellow precipitate, was recrystallized three times from water and air-dried at room temperature for more than one week. Yellow crystals; yield 2.8 g (56%); dp 292 °C; ep 340 °C. No further significant change of weight (>1%) was observed for at least 85 d.

Undecahydrates of the Light Lanthanoids (Ce-Gd) and Octahydrates of the Heavy Lanthanoids (Dy, Yb). These were prepared from picric acid and the corresponding carbonate as above, typically using 15 mmol of the former and 2.5 mmol of the latter. They are all yellow crystals; their yields and decomposition and explosion points are given in Table 1.

In order to check the contamination of unreacted picric acid, the crystalline lanthanoid picrates obtained above were extracted with dichloromethane. A spectral examination of the dichloromethane extracts did not show any absorbance greater than 0.01 at wavelengths >290 nm; therefore, the samples were free from picric acid. Aqueous solutions of La-Gd, Dy, and Yb picrates all showed absorption maxima at an identical wavelength of 354 nm with very close absorption coefficients (Table 1). The coefficients around 42000 $M^{-1}cm^{-1}$ are reasonable in view of those for alkali metal picrates (14400—14800 $M^{-1}cm^{-1}$) and for alkaline earth metal picrates (29100—31000 $M^{-1}cm^{-1}$).

The IR spectra of light lanthanoid picrate undecahydrates (La-Gd) are all superimposable with respect to the frequencies and relative intensities of their peaks: ν(KBr) 3400 (br), 3090, 1635, 1615, 1565, 1560, 1500, 1485, 1440, 1370, 1335, 1280, 1270, 1240, 1165, 1080, 940, 905, 795, 745, 710, 705, 545, 520 cm^{-1}. The heavy lanthanoid picrate octahydrates (Dy, Yb) also exhibit quite analogous spectra but evidently weaker absorption at 3400 cm^{-1}; ytterbium picrate possesses a broadened 3400 cm^{-1} band and two additional weak absorptions at 1425 and 1405 cm^{-1}. These spectra are essentially identical as that of sodium picrate monohydrate[4] or calcium picrate pentahydrate[3,5] except for the intensity of the O-H stretching band around 3400 cm^{-1}.

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