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Rare-Earth Metal Methanephosphonates

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Abstract—Addition of a KOH solution to aqueous solutions containing methanephosphonic acid H_2L and rare-earth ions Ln^{3+} results in crystallization of $LnHL_2$ (Ln = La–Er, Y) and $KLn_3H_6L_8$ (Ln = Yb, Lu); Tm forms the salts of both types. The solubility and thermal stability of the products were studied.

From aqueous solutions containing rare-earth ions Ln^{3+} and alkanephosphonic acids RPO_3H_2 (H_2L), various compounds were isolated: $Ln(RPO_3H)_3 \cdot nH_2O$ {H_2L = $C_6H_5C(CH_2)PO_3H_2$ [1], $CH_3CH(NH_2)CH_2 \cdot PO_3H_2$ [2]}, $LnHL_2 \cdot nH_2O$ (H_2L = $HOC_6H_4OCH_2 \cdot PO_3H_2$ [3]), and $Ln_2L_3 \cdot nH_2O$ {H_2L = $C_6H_5PO_3H_2$, $C_6H_5C(CH_2)PO_3H_2$ [1], $C_6H_5C(OH)(CH_3)PO_3H_2$ [4]}. Also, neodymium alkanephosphonates $NdHL_2$ are known (H_2L = $CH_3PO_3H_2$, $ClCH_2PO_3H_2$, $C_7H_{15} \cdot PO_3H_2$, $C_8H_{17}PO_3H_2$) [5].

Here, we report the preparation and some properties of methanephosphonates (H_2L = $CH_3PO_3H_2$) of rare-earth elements (Ln = La, Nd, Sm, Gd, Dy, Er, Tm, Yb, Lu, and Y).

On adding a KOH solution to aqueous solutions of the composition $3CH_3PO_3H_2$ + $LnCl_3$ (Ln = La–Er, Y) (pH < 3), dense finely crystalline precipitates of $LnHL_2$ are gradually formed (see table). The same compounds crystallize with NaOH or NH_4OH used instead of KOH, and also upon alkalization of solutions with other reactant ratios: $4CH_3PO_3H_2$ + $LnCl_3$ and $CH_3PO_3H_2$ + $2LnCl_3$. The fact that the precipitate composition is independent of the reactant ratio and the base used for neutralization suggests that the rare-earth metal methanephosphonates obtained are individual compounds.

A different pattern is observed with Yb and Lu. Addition to solutions containing $CH_3PO_3H_2$ and $LnCl_3$ (molar ratio from 4 : 1 to 1 : 2) of a KOH solution up to the onset of crystallization (pH < 3) results in formation of loose precipitates consisting of hexagonal plates; their most probable composition, according to elemental analysis, is $KLn_3H_6L_8$. As expected, the precipitate composition changes when NaOH or NH_4OH is used instead of KOH.

By adding to a $3CH_3PO_3H_2$ + $TmCl_3$ solution KOH in portions up to the onset of crystallization and taking fractions of the precipitate, it is possible to isolate first $KTm_3H_6L_8$ and then $TmHL_2$ (see table).

On adding a drop of a KOH solution to an $nCH_3 \cdot PO_3H_2$ + $LnCl_3$ solution, a gelatinous precipitate is formed, which quickly dissolves on stirring. The last added drop of the KOH solution gives a precipitate dissolving very difficultly. From the resulting solutions, the above-described crystalline rare-earth metal methanephosphonates precipitate gradually. Due to complexation of Ln^{3+} with $CH_3PO_3H_2$ [6] and formation of a solid phase, the solution pH decreases, and the product yield is low. The repeated careful alkalization (until the initially formed precipitate ceases to dissolve on stirring) yields an additional crop of a well-crystallized secondary precipitate, identical in the composition to the precipitate of the first fraction. The total number of moles of the alkali added per mole of methanephosphonic acid does not exceed 1, so that the reaction mixture remains strongly acidic.

$$2CH_3PO_3H_2 + LnCl_3 \rightleftarrows LnH(CH_3PO_3)_{2\downarrow} + 3HCl,$$

$$Ln = La—Er,\ Y.$$

$$7CH_3PO_3H_2 + CH_3PO_3HK + 3LnCl_3$$

$$\rightleftarrows KLn_3H_6L_{8\downarrow} + 9HCl,$$

$$Ln = Yb,\ Lu.$$

The acidic medium ensures a low crystallization rate. When $nCH_3PO_3H_2$ + $LnCl_3$ mixtures are quickly neutralized to pH 4–6 with solutions of MOH (M = Na, K, NH_4) or hexamethylenediamine, gels stable for a long time are formed.

The compounds $LnHL_2$ (Ln = La–Tm, Y) are finely crystalline colorless or pale-colored substances; their color corresponds to the color of the corresponding Ln^{3+} aqua ions (see table). The compounds $KLn_3H_6L_8$ (Ln = Tm–Lu) are colorless substances crystallizing in the form of hexagonal plates. The

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Analytical data for rare-earth metal methanephosphonates

Compound	Found, %		Formula	Calculated, %	
	Ln	P		Ln	P
$LaHL_2$[a]	41.5	18.9	$C_2H_7LaO_6P_2$	42.36	18.89
$NdHL_2$[b]	42.9	18.5	$C_2H_7NdO_6P_2$	43.28	18.59
$SmHL_2$[a]	43.9	18.4	$C_2H_7O_6P_2Sm$	44.31	18.25
$GdHL_2$[a]	45.2	17.6	$C_2H_7GdO_6P_2$	45.41	17.89
$DyHL_2$	46.0	17.2	$C_2H_7DyO_6P_2$	46.23	17.68
$ErHL_2$[c]	46.5	17.3	$C_2H_7ErO_6P_2$	46.95	17.39
$TmHL_2$[a]	47.5	17.0	$C_2H_7O_6P_2Tm$	47.19	17.30
$KTm_3H_6L_8$[a]	39.4	19.1	$C_8H_{30}KO_{24}P_8Tm_3$	38.86	19.00
$KYb_3H_6L_8$[a]	39.5	18.9	$C_8H_{30}KO_{24}P_8Yb_3$	39.43	18.82
$KLu_3H_6L_8$[a]	39.9	18.9	$C_8H_{30}KLu_3O_{24}P_8$	39.70	18.74
YHL_2[a]	32.0	22.0	$C_2H_7O_6P_2Y$	31.99	22.29

[a] Colorless. [b] Lilac. [c] Pink.

compounds are soluble in mineral acids and in an Na_2EDTA solution (on heating) and sparingly soluble in water (the solubility sharply increases at low pH, Fig. 1), aqueous alkalis and ammonia, DMSO, DMF, acetic acid, glycerol, ethanol, acetone, dioxane, CCl_4, and benzene. The substances are nonhygroscopic. X-ray diffraction patterns show that $LnHL_2$ are well-crystallized substances with a strong texture.

The IR spectra and thermal analysis confirm that the compounds are anhydrous. For example, the weight loss (%) on heating at 150°C to constant weight is as small as 0.07 (La), 0.18 (Nd), 0.56 (ðr), 0.36 (Y), 0.20 (Yb), and 0.15 (Lu) and is due to removal of adsorbed water. The compounds show a high thermal stability: The methanephosphonate anion starts to decompose only at 400–430°C, and the weight loss in this stage is as small as 2.5–4.5% (Fig. 2). The stability increases in the order Lu ≈ Yb < La < Er < Nd ≈ Sm. Heating above 550–570°C causes a more profound degradation, with carbonization and release of large amounts of gaseous pyrolysis products (Fig. 2).

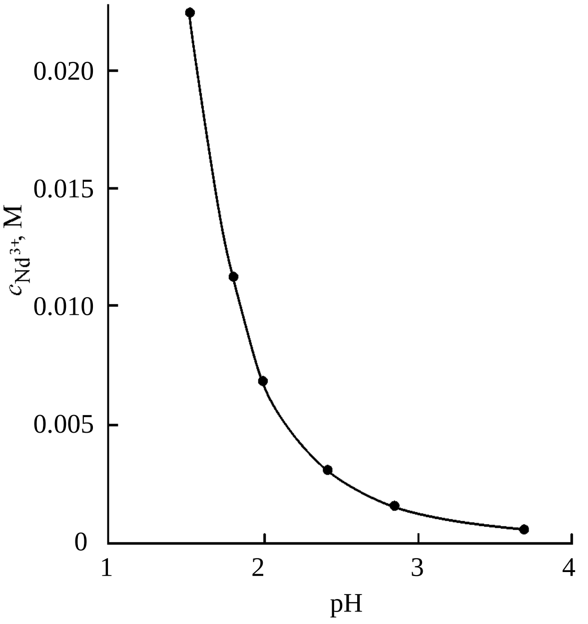

Fig. 1. Solubility of $NdHL_2$ in water at 25°C as a function of pH.

EXPERIMENTAL

Methanephosphonic acid was prepared by hydrolysis of methanephosphonic dichloride. The acid concentration in aqueous solution was determined by alkali titration with methyl red and thymolphthalein as indicators. The Ln^{3+} solutions were prepared from

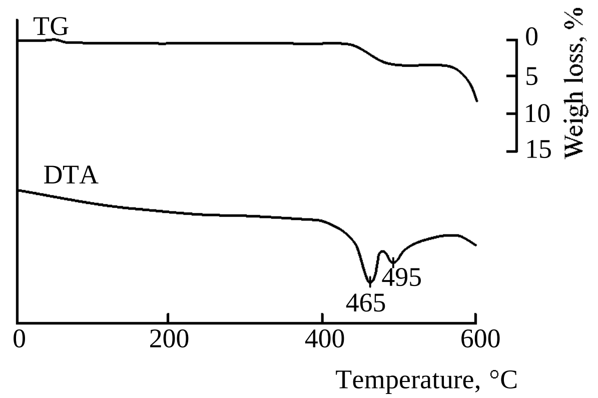

Fig. 2. TG and DTA curves for $NdHL_2$.

chemically pure grade $LnCl_3 \cdot nH_2O$; their concentration was determined by complexometric titration. The thermal anlaysis was performed on an OD-103 derivatograph (100-mg sample, quartz crucible) in an N_2 atmosphere at a heating rate of 6 deg min^{-1} in the range 20 – 600°C. To detect more precisely the onset of thermal decomposition of the anion, the product obtained by calcination at a given temperature in an inert atmosphere for 1 h was heated first with 2 M HNO_3 and then with molybdate solution and NH_4NO_3. Formation of the precipitate of ammonium phosphomolybdate is indicative of the occurrence of $CH_3PO_3^{2-}$ pyrolysis. The Ln content was determined complexometrically by back titration of excess Na_2EDTA with a solution of $CuSO_4$ in hexamethylenetetramine buffer (pH 5– 6) at ~60 –80°C (xylenol orange indicator). The phosphorus content was determined gravimetrically in the form of quinolinium phosphomolybdate [7] after oxidation of methanephosphonate to orthophosphate (fusion of the complex with $NaNO_3$ at 500 –550°C [8]). To determine the solubility, water was acidified with the required amount of HCl and mixed with the $NdHL_2$ powder until a constant Nd^{3+} concentration was attained, and the equilibrium pH was registered.

Rare-earth metal methanephosphonates. A 1.0 M solution of $CH_3PO_3H_2$ (15 ml) was mixed with a 0.50 M solution of $LnCl_3$ (10 ml). A 1.0 M KOH solution was added dropwise with stirring until the initially forming precipitate ceased to dissolve, and the resulting solution was filtered if necessary. The precipitate that formed within several days was vacuum-filtered through a glass frit, washed with three portions of water and then with acetone, and dried in air at room temperature to constant weight. An additional crop of the product was isolated from the filtrate by adding a KOH solution dropwise until the initially formed gelatinous precipitate ceased to dissolve on stirring; the pH was kept below 3.

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