Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 901–902. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 964–965.

Rare-Earth Chloromethanephosphonates

E. G. Afonin

Khimiko-tekhnologicheskaya laboratoriya, State Enterprise, Kaluga, Russia

Received September 18, 2000

Abstract—Addition of KOH to aqueous solutions containing in a 3 : 1 molar ratio chloromethanephosphonic 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). According to powder diffraction patterns, all the compounds within the $LnHL_2$ and $KLn_3H_6L_8$ groups are isostructural. Thulium forms a mixture of these two compounds. The solubility, IR spectra, and thermal stability of the products were studied.

Chloromethanephosphonic acid $ClCH_2PO_3H_2$ (H_2L) in aqueous solution at low pH forms with Nd^{3+} ions the complex $ClCH_2PO_3HNd^{2+}$ (K_{stab} 8.3) [1]. Addition of an alkali to the acid solution results in crystallization of $NdHL_2$ [2]. Here we report the synthesis of rare-earth chloromethanephosphonates (Ln = La, Pr, Nd, Eu, Gd, Dy, Er, Tm, Yb, Lu, and Y) and their study by elemental analysis, powder X-ray diffraction, thermal analysis, and IR spectroscopy.

Mixing of aqueous solutions of $ClCH_2PO_3HK$ and $LnCl_3$ (molar ratio 3 : 1) results in precipitation of crystals which, according to elemental analysis, have the compositions $LnHL_2$ for Ln = La–Er and Y and $KLn_3H_6L_8$ for Ln = Yb and Lu (see table). At the same time, mixing of solutions of $ClCH_2PO_3K_2$ and $LnCl_3$ in various molar ratios yields gels stable for a long time.

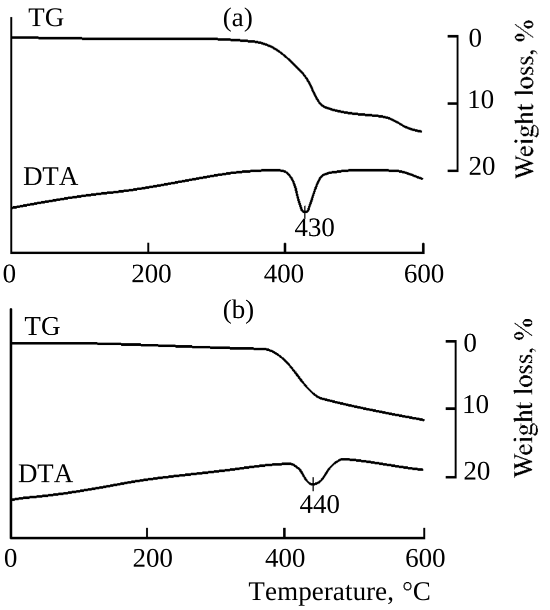
The color of rare-earth chloromethanephosphonates is similar to the color of the corresponding Ln^{3+} aqua ions (see table). The compounds are soluble in mineral acids and aqueous EDTA solution (on heating) and poorly soluble in water, aqueous ammonia, alkalis, DMSO, DMF, acetic acid, glycerol, ethanol, dioxane, carbon tetrachloride, and benzene. The compounds are nonhygroscopic.

According to powder X-ray diffraction patterns, Ln chloromethanephosphonates show high crystallinity and pronounced texture. The compounds $LnHL_2$ (Ln = La–Er) are isostructural, and the compounds $KLn_3H_6L_8$ (Ln = Yb, Lu) have different diffraction patterns, being isostructural with each other. YHL_2, according to the X-ray diffraction pattern, is isostructural with $LnHL_2$; Tm forms a mixture of both forms, with $KTm_3H_6L_8$ prevailing.

Analytical data for rare-earth chloromethanephosphonates

Compound	Found, %			Formula	Calculated, %		
	Cl	Ln	P		Cl	Ln	P
$LaHL_2$[a]	17.2	35.6	15.0	$C_2H_5Cl_2LaO_6P_2$	17.87	35.00	15.61
$PrHL_2$[b]	17.6	35.2	15.7	$C_2H_5Cl_2O_6P_2Pr$	17.78	35.33	15.53
$NdHL_2$[c]	17.4	36.2	15.2	$C_2H_5Cl_2NdO_6P_2$	17.63	35.87	15.40
$EuHL_2$[a]	17.0	37.5	15.0	$C_2H_5Cl_2EuO_6P_2$	17.30	37.07	15.11
$GdHL_2$[a]	17.0	38.0	14.6	$C_2H_5Cl_2GdO_6P_2$	17.08	37.88	14.92
$DyHL_2$[a]	16.9	38.9	14.3	$C_2H_5Cl_2DyO_6P_2$	16.87	38.65	14.73
$ErHL_2$[d]	16.9	40.0	14.2	$C_2H_5Cl_2ErO_6P_2$	16.68	39.34	14.57
$KYb_3H_6L_8$[a]	16.9	32.8	15.5	$C_8H_{22}Cl_8KO_{24}P_8Yb_3$	17.82	32.61	15.57
$KLu_3H_6L_8$[a]	17.0	32.9	15.2	$C_8H_{22}Cl_8Lu_3KO_{24}P_8$	17.75	32.85	15.51
YHL_2[a]	20.0	26.0	17.2	$C_2H_5Cl_2O_6P_2Y$	20.44	25.63	17.86

[a] Colorless. [b] Yellow-green. [c] Lilac. [d] Pink.



TG and DTA curves for (a) $PrHL_2$ and (b) $DyHL_2$.

Thermal analysis confirms that the compounds are anhydrous. For example, the weight loss due to removal of adsorbed water on heating at 180°C to constant weight is as small as 0.67 (La), 0.37 (Pr), and 0.37% (Lu). The compounds show high thermal stability (see figure): the chloromethanephosphonate anion starts to decompose only at 370–400°C [endothermic effects (DTA) at 430°C], with the initial weight loss of 9–10%.

The change in the chemical form of chloromethanephosphonates in going from Er to Yb, revealed by elemental analysis and powder X-ray diffraction, is reflected in the IR spectra. The spectra of $LnHL_2$ are virtually similar but differ considerably from those of $KLn_3H_6L_8$ in both the number and positions of absorption bands [except $\nu(CH_2)$]. The most pronounced differences are observed in the range 1200–900 cm^{-1} as a result of differences in the degree of protonation of phosphonate groups and in the hydrogen bonding pattern.

EXPERIMENTAL

Chloromethanephosphonic acid was prepared by hydrolysis of its dichloride. The concentration of H_2L in aqueous solution was determined by alkali titration with pH-potentiometric detection of the equivalence point. Solutions of Ln^{3+} were prepared from $LnCl_3 \cdot nH_2O$ (chemically pure grade); the concentrations were determined by complexometric titration. Powder X-ray diffraction patterns were obtained with a DRON-3.0 diffractometer (CuK_α radiation). Thermal analysis was performed with an OD-103 derivatograph (100-mg sample, quartz crucible) under N_2 at a heating rate of 6 deg min^{-1} in the range 20–600°C. The IR spectra (mulls in mineral oil and in hexachlorobutadiene) were taken on a UR-20 spectrometer in the range 4000–400 cm^{-1}. Analysis for Ln was performed complexometrically [back-titration of excess Na_2EDTA solution 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 with quinolinium phosphomolybdate [3], and that of chlorine, by argentometric titration preceded by decomposition of chloromethanephosphonate to orthophosphate and chloride (fusion with $NaNO_3$ at 500–550°C) [4].

Rare-earth chloromethanephosphonates were prepared by mixing 15-ml portions of 1.0 M solutions of $ClCH_2PO_3H_2$ and KOH and subsequently adding with stirring 5 ml of 1.0 M $LnCl_3$ solution. After several days, the precipitate was filtered off on a glass frit at reduced pressure, washed with three portions of water and then with acetone, and dried in air at room temperature to constant weight.

ACKNOWLEDGMENTS

The author is grateful to A.N. Bovin (Institute of Physiologically Active Substances, Russian Academy of Sciences) and A.V. Kamchatkin (Moscow State University) for assistance.

REFERENCES

1. Afonin, E.G., Chepaikina, T.A., Isaeva, E.V., and Pechurova, N.I., *Vestn. Mosk. Gos. Univ., Ser. 2: Khim.*, 1989, vol. 30, no. 4, pp. 364–368.
2. Afonin, E.G., Chepaikina, T.A., and Pechurova, N.I., *Zh. Neorg. Khim.*, 1989, vol. 34, no. 9, pp. 2254–2256.
3. Williams, W.J., *Handbook of Anion Determination*, London: Butterworth, 1979.
4. Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry*, Glasgow: Int. Textbook, 1978.