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LETTERS TO THE EDITOR

Synthesis, Acid–Base and Complexing Properties of Tripotassium Tributyl [Nitrilotris(methylene)]tris(phosphonate)

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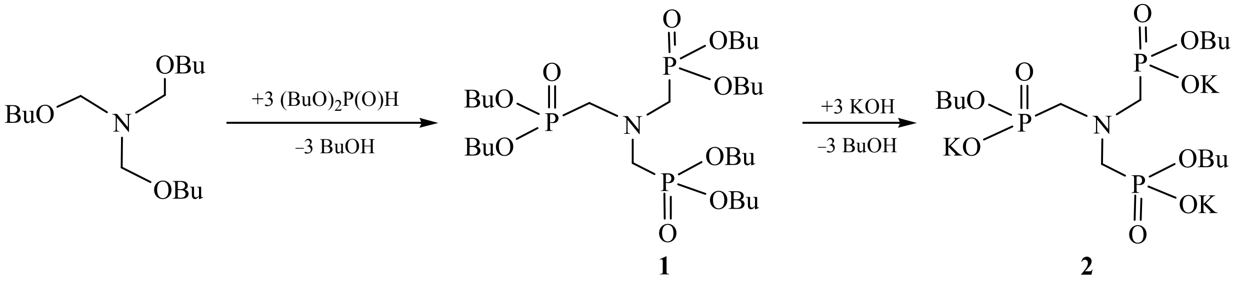
We previously demonstrated high efficiency of membrane extraction of lithium ions from their mixtures with other alkali metals using a new synergic aminophosphoryl carrier, a mixture of hexapentyl [nitrilotris(methylene)]tris(phosphonate) and *O*,*O*-bis-(2-ethylhexyl) hydrogen phosphorothioate [1]. Herein we report the results of studying acid–base and complexing properties toward transition metal ions of a new tris(phosphorylmethyl)amine, tripotassium tributyl [nitrilotris(methylene)]tris(phosphonate) (**2**) which was synthesized by alkaline hydrolysis of the corresponding hexabutyl tris-phoshonate **1** with aqueous potassium hydroxide (Scheme 1). The latter was prepared in turn by reaction of tris(butoxymethyl) amine with 3 equiv of dibutyl phosphonate according to the procedure described in [2].

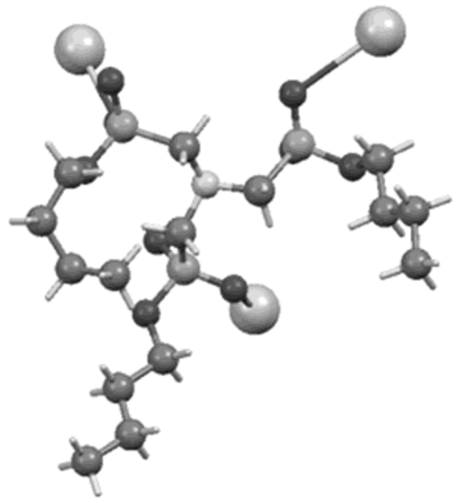
The structure of tripotassium salt **2** was determined on the basis of ^{1}H, ^{13}C–{^{1}H}, and ^{31}P–{^{1}H} NMR and X-ray diffraction data (see figure). The ionization constants of tributyl [nitrilotris(methylene)]tris(hydrogen phosphonate) in water were determined by potentiometric titration of a solution of **2** with a 0.1 M solution of nitric acid: $pK_1 = 1.02$, $pK_2 = 1.29$, $pK_3 = 6.25$.

Salt **2** was found to form water-soluble complexes with manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) ions. The stability constants (log β) of the corresponding 1 : 1 complexes were estimated by potentiometric titration at 3.76, 4.96, 3.87, 7.25, and 6.37 for Mn(II), Co(II), Ni(II), Co(II), and Zn(II), respectively. This log β series is very consistent with the Irving–Williams series with the exception that the stability constant of the nickel complex is lower than the stability constant of analogous cobalt complex [3].

Hexabutyl [nitrilotris(methylene)]tris(phosphonate) (1). An Arbuzov flask equipped with a thermometer, capillary, bent vacuum-distilling adapter, and graduated test tube receiver was charged with 0.17 mol (47.77 g) of tris(butoxymethyl)amine and 0.52 mol (100.98 g) of dibutyl phosphonate, four drops of saturated *p*-toluenesulfonic acid in toluene were added, and the mixture was heated for 3 h at 110°C at a residual pressure of 22 mm (until butan-1-ol no longer distilled off). The residue was a colorless viscous oil which was almost pure tris-phosphonate **1**. Yield 96%, $n_D^{20} = 1.4515$. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz): 0.95 t (18H, CH$_3$, $^{3}J_{HH} = 7.4$), 1.36–1.46 m (12H, CH$_2$), 1.60–1.67

Scheme 1.





Structure of the molecule of tripotassium tributyl [nitrilotris(methylene)]tris(phosphonate) (**2**) in crystal according to the X-ray diffraction data.

m (12H, CH_2), 3.31 d (6H, PCH_2N, $^2J_{PH}$ = 10.9), 4.02–4.09 m (12H, OCH_2). ^{31}P NMR spectrum: δ_P 23.94 ppm.

Tripotassium tributyl [nitrilotris(methylene)]tris (phosphonate) (2). A mixture of 108 g (0.17 mol) of tris-phosphonate **1** and 71 g of 50% aqueous potassium hydroxide (0.52 mol) in 25 mL of dioxane was heated for 6 h at 110°C. When the reaction was complete (^{31}P NMR), the mixture was cooled, and the white plates were filtered off and recrystallized from ethanol–acetone (1 : 2). Yield 57.3 g (51.2%), decomposition point 230°C. IR spectrum, ν, cm^{-1}: 1215 (P=O), 1046 (P–O–C). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 0.86 t (9H, CH_3, $^3J_{NH}$ = 7.4), 1.28–1.37 m (6H, CH_2), 1.52–1.58 m (6H, CH_2), 3.01 d (6H, PCH_2N, $^2J_{PH}$ = 11.1), 3.82–3.87 m (6H, OCH_2). $^{13}C–\{^1H\}$ NMR spectrum (D_2O), δ_C, ppm (*J*, Hz): 13.1 [$(CH_2)_3\underline{C}H_3$], 18.4 [$(CH_2)_2\underline{C}H_2CH_3)$], 32.3 d ($CH_2\underline{C}H_2CH_2CH_3$, $^3J_{PC}$ = 5.6), 52.5 d (PCH_2, $^1J_{PC}$ = 150.0), 64.6 d [$\underline{C}H_2(CH_2)_2CH_3$, $^2J_{PC}$ = 5.8]. $^{31}P–\{^1H\}$ NMR spectrum (D_2O): δ_P 20.74 ppm. Found, %: K 20.15. $C_9H_{21}K_3NO_9P_3$. Calculated, %: K 20.17.

The ^1H, $^{13}C–\{^1H\}$, and $^{31}P–\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at 400, 100, and 160 MHz, respectively. The ^1H chemical shifts were measured relative to the residual proton signals of the deuterated solvents ($CDCl_3$, D_2O). The IR spectra were recorded on a Perkin Elmer UATR Two FT-IR Spectrometer (Spectrum Two). The melting (decomposition) points were determined with an accuracy of ±1°C with a Stuart SMP10 melting point apparatus. Potentiometic measurements were performed at 25°C using an EKSPERT-001 instrument equipped with an ES-10603 glass electrode (measurement accuracy ±0.001 pH unit; experimental error ±0.005 pH unit) and an ESr-10108 silver chloride electrode. The results were processed using CPESSP software [4].

The X-ray diffraction data for compound **2** were acquired at 198(2) K on a Bruker AXS Kappa APEX Duo diffractometer (CuK_α radiation, λ 1.54178 Å) using APEX2 [5], SAINT [6], SHELXS97 [7], and SADABS [8]. Orthorhombic crystal system, space group *Pbca*; $C_{13}H_{10}K_3N_3O_{11}P_3$, *M* 584.37; unit cell parameters: a = 18.1114(7), b = 9.3665(4), c = 33.2472(13) Å; V 5640.1(4) $Å^3$; Z = 8; d_{calc} = 1.376 g/cm^3; μ = 6.365 mm^{-1}. Total of 52 285 reflection intensities were measured, including 5168 independent reflections (R_{int} = 0.0446) and 5125 reflections with $I \geq 2\sigma(I)$; 298 variables; R = 0.0575, wR^2 = 0.1687; maximum/minimum residual electron density 1.183/–0.583 $\bar{e}/Å^{-3}$. The crystallographic data for compound **2** were deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 1 489 195).

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