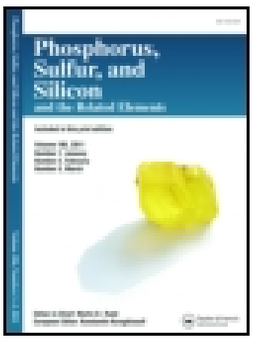

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SHORT COMMUNICATION

Synthesis and complexation of N,N-Bis(O-diethylhydroxyphosphorylmethyl)-N-butylamine

Rafael A. Cherkasov[a], Igor D. Shurygin[a], Airat R. Garifzyanov[a], Ildar I. Mirzayanov[a], Aynaz Z. Gaynullin[a], Kamil A. Ivshin[a], and Olga N. Kataeva[b]

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ABSTRACT

The acid-base and complexing properties of N,N-bis(O-diethylhydroxyphosphorylmethyl)-N-butylamine (H_3L) with divalent metals were investigated in aqueous solution via the potentiometric titration method. The formation of 1:1 species has been established. The structure of complex N,N-bis(O-diethylhydroxyphosphorylmethyl)-N-butylamine with copper(II) was determined using an X-ray diffraction method.

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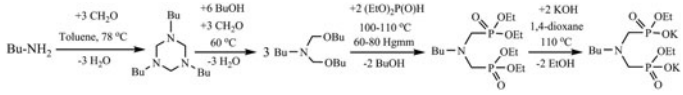
KEYWORDS
Acid-base properties; aminophosphonates; stability constants; complexation

GRAPHICAL ABSTRACT



Organophosphorus chelating agents are widely used in many applications. Herein we report our investigations of complexing properties of N,N-bis(O-diethylhydroxyphosphorylmethyl)-N-butylamine (H_3L).

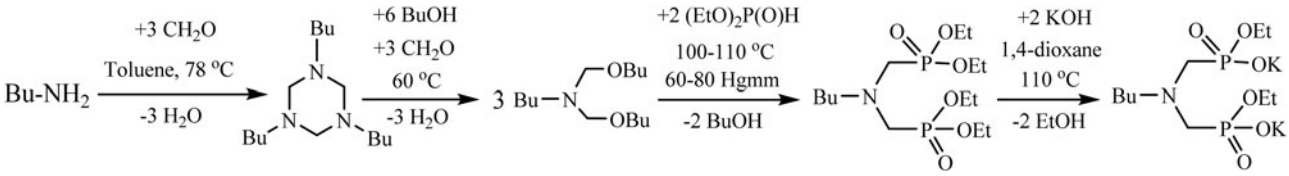
Potassium salt of H_3L was synthesized according to the following Scheme 1:

The dissociation constants (pK_1 and pK_2 for phosphonic acid groups, pK_3 for amino group) of H_3L having the values pK_1 1.05, pK_2 1.20, and pK_3 7.74 were determined via the potentiometric titration. During the complexation research of H_3L with divalent metal's ions in aqueous solution at the pH values between 1.5 and 9 at a molar ratio of metal to ligand is 1:1, there are only MHL and ML^- complexes. The stability constants are presented in Table 1.

The mononuclear complex species ML^- are predominant at the neutral and alkaline solutions, while MHL species occur at the acidic solutions. Complexes' destruction begins with nitrogen atom protonation leading to the opening of five-membered rings.

The complex N,N-bis(O-diethylhydroxyphosphorylmethyl)-N-butylamine with copper(II) (Figure 1 was synthesized by addition of a copper(II) nitrate solution (5 mL (0.1 mol/L)) to a H_3L (5 mL (0.1 mol/L)) solution. The mixture was kept in an open vessel at room temperature for 2 months.

This study was performed under financial support by the state subsidy allocated for Kazan Federal University for its competitive growth.



Scheme 1. Synthesis of N,N-bis(O-diethylhydroxyphosphorylmethyl)-N-butylamine.

Table 1. The stability constants of H3L complexes with divalent metal's ions.

LGB	MG^{2+}	CA^{2+}	SR^{2+}	BA^{2+}	MN^{2+}	CO^{2+}	NI^{2+}	CU^{2+}	ZN^{2+}	CD^{2+}
MHL	1.31	1.50	0.58	0.97	1.25	1.99	1.79	1.59	1.70	0.90
ML^-	1.71	1.85	1.02	1.17	2.76	3.47	3.50	5.98	3.76	3.96

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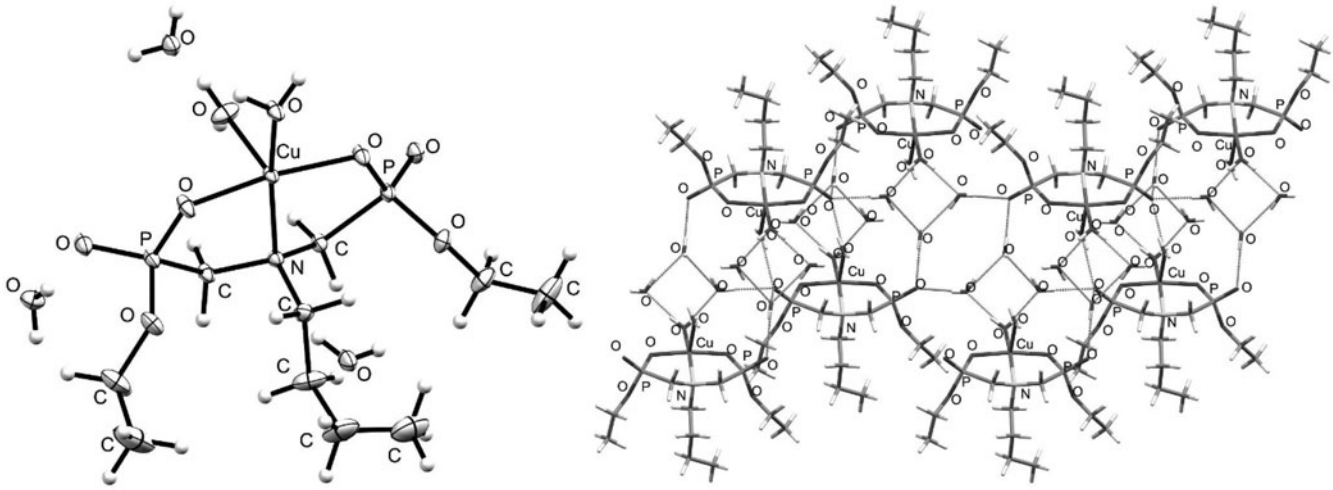

Figure 1. Crystal structure of complex N,N-bis(O-diethylhydroxyphosphorylmethyl)-N-butylamine with copper(II).

The ionic strength of all solutions was adjusted to 0.2 mol/L (KNO_3) and the temperature was maintained at 25.0 ± 0.1 °C. The pH values were measured with an Expert-001-2 instrument equipped with an ES-10603 glass electrode.

Data set for single crystal of $C_{10}H_{27}CuNO_8P_2{\cdot}3H_2O$ was collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at $T = 120(2)$ K. Crystal size $0.511 \times 0.405 \times 0.273$ mm^3. Programs used: data collection APEX3,[1] data reduction SAINT,[2] structure solution SHELXS,[3] structure refinement by full-matrix least-squares against F^2 using SHELXL.[3] CCDC 1868817 contains the supplementary crystallographic data for this paper.

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