

# Synthesis, crystal structure and vibrational spectra of the new strong and eco-friendly reducing agent $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_2)_2$

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## Abstract

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## Introduction

## Materials and Methods

### Materials

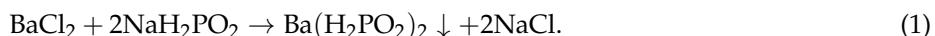
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  ( $\geq 98\%$ , Sigma-Aldrich, Milwaukee, WI, USA);  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  ( $\geq 99\%$ , Sigma-Aldrich, Milwaukee, WI, USA);  $\text{H}_2\text{SO}_4$ ;  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (64–65%,  $\geq 97\%$ , reagent grade Sigma-Aldrich, Milwaukee, WI, USA). All chemicals were used as purchased without further purification.

### Synthesis

Hydrazinium bishypophosphite  $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_2)_2$  was synthesized in two steps. Firstly a fresh aqueous solution of hypophosphorous acid is prepared from  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  and  $\text{H}_2\text{SO}_4$ . Then the acid is neutralized with hydrazine hydrate.

### Preparation of the precursor $\text{Ba}(\text{H}_2\text{PO}_2)_2$

Initially barium hypophosphite  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  was synthesized by mixing freshly prepared saturated aqueous solutions of  $\text{BaCl}_2$  and  $\text{NaH}_2\text{PO}_2$  at  $90^\circ\text{C}$ . After cooling to  $\sim 5^\circ\text{C}$  the reaction mixture was left for 2–3 h. Under these conditions  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  precipitates as a white crystalline product with high yield. The obtained white crystals were recrystallized from water, washed with cool water and dried in a desiccator.



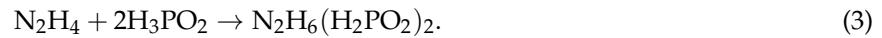
### Preparation of $\text{H}_3\text{PO}_2$ and $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_2)_2$

Aqueous solution of hypophosphorous acid  $\text{H}_3\text{PO}_2$  was prepared by dissolving barium hypophosphite  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  in cool water and slowly adding stoichiometric amount of  $\text{H}_2\text{SO}_4$  under constant stirring. A white crystalline product of  $\text{BaSO}_4$  precipitated immediately.



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The mixture was cooled down to  $\sim 5$  °C and left for 48 h to promote the Ostwald ripening of the small BaSO<sub>4</sub> crystals. Then the solution was filtered using a vacuum pump and the filtrate was used for the next step when stoichiometric amount of hydrazine hydrate was added to it under constant stirring.



The obtained hydrazinium hypophosphite salt is highly soluble in water and thus no visible change in the solution appearance was observed. The solution was evaporated slowly under vacuum ( $\sim 400$  mbar) at temperature of  $55 \pm 5$  °C.