# Synthesis, crystal structure and vibrational spectra of the new strong and eco-friendly reducing agent $N_2H_6(H_2PO_2)_2$

Ivo I. Lozanov[1]*, B. Morgenstern[2], M. Tsvetkov[1] and Lyudmil Lyutov[1,3]

[1]Department of Inorganic Chemistry, Faculty of Chemistry and Pharmacy, Sofia University 'St. Kliment Ohridski'
[2] Inorganic Solid State Chemistry, Saarland University, Campus Geb. C4 1, 66123 Saarbrücken, Germany; bernd.morgenstern@uni-saarland.de
[3] Institute of Metal Science with Hydro- and Aerodynamics Centre 'Acad. Angel Balevski'

**Abstract**

*j*

## Introduction

## Materials and Methods

### Materials

$BaCl_2 \cdot 2H_2O$ ($\geq$ 98%, Sigma-Aldrich, Milwaukee, WI, USA); $NaH_2PO_2 \cdot H_2O$ ($\geq$ 99%, Sigma-Aldrich, Milwaukee, WI, USA); $H_2SO_4$; $N_2H_4 \cdot H_2O$ (64-65%, $\geq$ 97%, reagent grade Sigma-Aldrich, Milwaukee, WI, USA). All chemicals were used as purchased without further purification.

### Synthesis

Hydrazinium bishypophosphite $N_2H_6(H_2PO_2)_2$ was synthesized in two steps. Firstly a fresh aqueous solution of hypophosphorous acid is prepared from $Ba(H_2PO_2)_2$ and $H_2SO_4$. Then the acid is neutralized with hydrazine hydrate.

### Preparation of the precursor $Ba(H_2PO_2)_2$

Initially barium hypophosphite $Ba(H_2PO_2)_2$ wa synthesized by mixing freshly prepared saturated aqueous solutions of $BaCl_2$ and $NaH_2PO_2$ at 90 °C. After cooling to $\sim$ 5 °C the reaction mixture was left for 2-3 h. Under these conditions $Ba(H_2PO_2)_2$ 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.

$$BaCl_2 + 2NaH_2PO_2 \rightarrow Ba(H_2PO_2)_2 \downarrow + 2NaCl. \quad (1)$$

### Preparation of $H_3PO_2$ and $N_2H_6(H_2PO_2)_2$

Aqueous solution of hypophosphorous acid $H_3PO_2$ was prepared by dissolving barium hypophosphite $Ba(H_2PO_2)_2$ in cool water and slowly adding stoichiometric amount of $H_2SO_4$ under constant stirring. A white crystalline product of $BaSO_4$ precipitated immediately.

$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow 2H_3PO_2 + BaSO_4 \downarrow . \quad (2)$$

*Corresponding author: ivoil@uni-sofia.bg

The mixture was cooled down to $\sim 5$ °C and left for 48 h to promote the Ostwald ripening of the small $BaSO_4$ 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.

$$N_2H_4 + 2H_3PO_2 \rightarrow N_2H_6(H_2PO_2)_2. \quad (3)$$

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.

## Computational protocol

To simulate the vibrational spectra of hydrazinium bishyphosphite several structural models were considered. The calculation were performed using several levels of theory including DFT, the wavefunction-based MP2 method, as well as hybrid and double-hybrid functionals. The used basis set was aug-cc-pVDZ to properly capture the weak intermolecular interactions. All calculations were performed using the Gaussian 09 software.