

# Environmentally Acceptable Synthesis Of Magnesium Bearing Fertilizers. III Solid State Synthesis

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**Abstract.** Nutrition is a key factor in human life and the development of civilization. The production of sufficient food requires the use of: efficient agricultural techniques, suitable soils and the use of nitrogen (N) fertilizers. However, the use of synthetic nitrogen fertilisers is associated with significant problems, caused by the fact that they are not sufficiently retained in soils to be taken up by plants and a significant proportion of the applied fixed nitrogen is lost. This is a serious economic problem for the farmers and a serious environmental problem for the society. In this work, the known methods for reducing the loss of bound nitrogen when fertilizer formulations are applied to the soil are discussed, and a promising preparation is presented, which is a complex of urea with magnesium sulfate, named magnesium sulfate hexaureate hemi hydrate,  $[\text{Mg}((\text{H}_2\text{N})_2\text{CO})_6] \text{SO}_4^{1/2} \text{H}_2\text{O}$ , which can find application both alone and in the formulation of the complex fertilizer formulations, as well as a convenient method for its preparation. The use of  $[\text{Mg}((\text{H}_2\text{N})_2\text{CO})_6] \text{SO}_4^{1/2} \text{H}_2\text{O}$ , instead of conventional nitrogen fertilisers, besides the reduction of losses of fixed nitrogen, is that it supplies the soil with the trace elements Mg and S. The low hygroscopicity and the good stability of the preparation are also essential. The known ureate complexes of magnesium sulphate and their preparation are discussed. The proposed new method of solid-phase synthesis, has certain advantages. The use of solid synthesis state methods has a number of advantages: solvent-free synthesis, low-temperature operation, high yields, and the absence of by-products make these methods the most environmentally acceptable.

**Keywords:** *fertilisers, nitrogen losses, magnesium sulphate, urea*

## I. INTRODUCTION

Food is a key factor in the development of civilization. Despite efforts to reduce food deficits, there are still hundreds of millions of people who are starving. An additional negative factor is the growing population of the earth, which has now reached 8 billion people. Despite the progress made, on average, between 1908 and 2008, the number of people living on 1 hectare of cultivable land increased by 200% [1]. Such an increase in agricultural productivity is impossible without the use of nitrogen (N) fertilizers. The use of synthetic N fertilizers, however, is associated with significant problems conditioned by the fact that they are not retained in soils sufficiently to be absorbed by plants and a significant portion of the applied fixed N is lost. In the first place to the atmosphere mainly as ammonia, but also as nitrogen and nitrogen oxides ( $\text{N}_2\text{O}$ ). Losses of bound nitrogen are estimated to be up to 40% of the amount applied. Zhenli& Kumar [2] give the following order of losses in the form of ammonia depending on the applied fertilizer in percentage:

$\text{NH}_4\text{CO}_3$ : 23.2;  $(\text{NH}_4)_2\text{SO}_4$ : 21.7;  $\text{CO}(\text{NH}_2)_2$ : 21.3;  $\text{NH}_4\text{NO}_3$ : 17.6

Additionally, losses are also caused by the processes of leaching and erosion. Losses can reach up to 70%, but it is accepted that more than half of the applied fixed nitrogen is lost during fertilization [3]. This is a serious economic problem for farmers and a serious environmental problem for society. The continuous use of synthetic (N) fertilizers, causes degradation of both soil and water ecosystems [4].

Therefore, the development of new strategies to reduce the losses of bound nitrogen during fertilizer application appears to be a priority task [5].

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One of the most commonly used nitrogen fertilizers, is urea. Approximately 60% of the bound nitrogen used for fertilization is applied as urea [6].

Various methods have been applied to reduce the losses of bound nitrogen when urea is used for fertilization:

- coverage of the urea fragments with a polymer shell;
- addition of the urease enzyme inhibitor NBPT (N-n-butyltriamide thiophosphate) or NPPT (reduce the rate of hydrolysis of urea in the soil and losses of bound nitrogen, but are ineffective in the presence of phosphorus fertilizer);
- addition of a porous component with a highly developed surface which immobilizes the active substance;
- other supplements: phosphogypsum (PG), diammonium phosphate,  $ZnSO_4$ ,  $NH_4Cl$  or  $KCl$

These approaches have different limitations. For example, the use of polymer-covered urea does not lead to an increase in nitrogen availability to plants in the soil, or to an increase in accumulated dry biomass compared to urea [7], [8], or phosphogypsum, depending on the apatite used in its preparation, which usually contains a large number of heavy metals that contaminate the soil.

One new highly efficient method to reduce the losses of bound nitrogen in fertilization is the use of urea complexes instead of pure urea. Typically, calcium or magnesium is used as a complex-forming reagent [9].

The use of magnesium solutions is definitely to be preferred because magnesium is an important bioelement and has a significant role in energy transfer in organisms and their absorption by plants. Figure 1, shows the reduction in losses of bound nitrogen as  $NH_3$  when  $[Mg((H_2N)_2CO)_6]SO_4 \cdot \frac{1}{2}H_2O$  is applied to a soil-fertilizer mixture relative to a urea control. The observed reduction is more than a doubling, which is an excellent result, higher than published results for urea complexes of calcium.

Currently there are more than 300 known enzyme systems in which magnesium ions are a cofactor, and which regulate various biochemical reactions in organisms participating in virtually all types of metabolism [10].

Magnesium is bound to ATP (adenosine triphosphate) and activates it, being the basis of energy transfer and the construction of ribonucleic acids [11].

Magnesium is involved in the structure of chlorophyll. In green plants, the magnesium ion is at the center of the porphyrin ring of chlorophyll [12] – the pigment that converts sunlight into absorbable energy by living organisms. Its presence in sufficient amounts in the environment is a necessary condition for efficient photosynthesis and growth.

Magnesium is an intracellular cation [13]. About 1% of the magnesium contained in multicellular organisms is located outside the cells. In plants, magnesium is mainly concentrated in chloroplasts.

On the other hand, many soils and crops are deficient in magnesium and require its application as fertilizer.

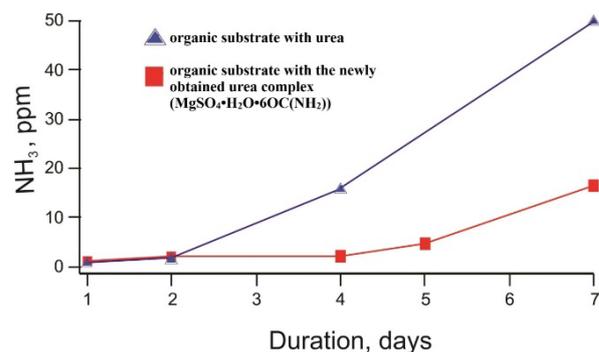


Fig. 1 Losses of bound nitrogen in the form of  $NH_3$  due to the application of  $[Mg((H_2N)_2CO)_6]SO_4 \cdot \frac{1}{2}H_2O$  and  $(H_2N)_2CO$  in a soil-fertilizer mixture [33].

## II. MATERIAL AND METHODS

It was used:  $MgSO_4 \cdot 7H_2O$  - Fluka, Pour analyse and urea - Fluka, puriss.

### Obtaining $[Mg((H_2N)_2CO)_6]SO_4 \cdot \frac{1}{2}H_2O$

2.46 g ( $10^{-2}$ mol)  $MgSO_4 \cdot 7H_2O$  and 3.6 g ( $6 \cdot 10^{-2}$ mol)  $(H_2N)_2CO$  are placed in an agate mortar and are grinded for two or three minutes. The resulting semi-liquid paste is transferred to a beaker and placed in a thermostat at  $60^\circ C$ . The sample is placed in the oven and left to stand for 48 hours to complete the reaction and for drying. The resulting of  $[Mg((H_2N)_2CO)_6]SO_4 \cdot \frac{1}{2}H_2O$  is characterized by XRD and IR spectroscopy.

### Obtaining $[Mg(H_2O)((H_2N)_2CO)_4(SO_4)]$

2.46 g ( $10^{-2}$ mol)  $MgSO_4 \cdot 7H_2O$  and 2.4 g ( $4 \cdot 10^{-2}$ mol)  $(H_2N)_2CO$  are placed in an agate mortar and are grinded for two or three minutes. The resulting semi-liquid paste is transferred to a beaker and placed in a thermostat at  $60^\circ C$ . The sample is placed in the oven and left to stand for 48 hours to complete the reaction and for drying. The resulting of  $[Mg(H_2O)((H_2N)_2CO)_4(SO_4)]$  is characterized by XRD and IR spectroscopy.

### Obtaining $Mg(H_2N)_2CO(H_2O)_xSO_4$ ( $x=2;3$ )

2.46 g ( $10^{-2}$ mol)  $MgSO_4 \cdot 7H_2O$  and 600 mg ( $10^{-2}$ mol)  $(H_2N)_2CO$  are placed in an agate mortar and are grinded for two or three minutes. The resulting semi-liquid paste is transferred to a beaker and placed in a thermostat at  $60^\circ C$ . The sample is placed in the oven and left to stand for 48 hours to complete the reaction and for drying. The resulting of  $Mg(H_2N)_2CO(H_2O)_2SO_4$  and  $Mg(H_2N)_2CO(H_2O)_3SO_4$  are characterized by XRD and IR spectroscopy.

### IR spectroscopy

Infrared spectra were measured using Tensor 37 (Bruker) FT-IR spectrometer with  $4\text{ cm}^{-1}$  spectral resolution after averaging 128 scans on standard KBr pallets in the spectral region 500-4000  $\text{cm}^{-1}$  at room temperature.

### Powder X-ray diffraction (PXRD)

Powder XRD patterns of the studied samples were recorded on Empyrean Powder X-ray diffractometer (Malvern Panalytical, Netherlands) in the  $5^\circ - 90^\circ$   $2\theta$  range, scanning time 15min, using Cu radiation ( $\lambda =$

1.5406 Å) and PIXcel3D detector. Phase identification was carried out using the HighScore Plus program [35] and/or through X-ray powder diffraction patterns simulated on the basis of the single-crystal studies for each of the studied complex salts using the PowderCell program [36]. The semi-quantitative phase analysis was also conducted in the same environments.

### III. RESULTS AND DISCUSSION

The important role of the bioelement magnesium determines efforts to study its coordination chemistry. The preferred coordination number of magnesium is six. This applies both to solutions where the magnesium ion is coordinated by six solvent molecules in the first coordination sphere [14] and to the vast majority of known crystalline phases of magnesium ligands [15]. The solvation of the magnesium cation has been modeled repeatedly using methods ranging from molecular mechanics to rudimentary quantum calculations [16]. The preferred coordination number of 6 is easily explainable by considering that the magnesium cation coordinates through the unoccupied  $sp^3d^2$  hybrid orbitals that point to the octahedron vertices. Figure 2 shows their location in the lattice as well as the typical magnesium envelope in its complexes.

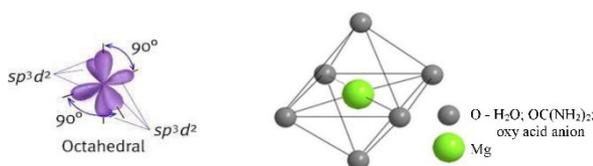


Fig. 2 Spatial distribution of the  $sp^3d^2$  orbitals of the magnesium cation and a typical octahedron coordination of magnesium.

The object of study in this work is the urea complexes of magnesium, so in the further discussion we will focus on them. The urea molecule has a simple and compact planar structure [17]. The heavy atoms are arranged in a single plane and are in the  $sp^2$  hybrid state. The structure of urea is schematically represented in Figure 3. The oxygen atom has two free electron pairs suitable for the formation of donor-acceptor bonds. They are located on nonbonding  $sp^2$  hybrid orbitals, located in the same plane and form an angle  $\Theta \approx 120^\circ$  with the double bond of the urea molecule.

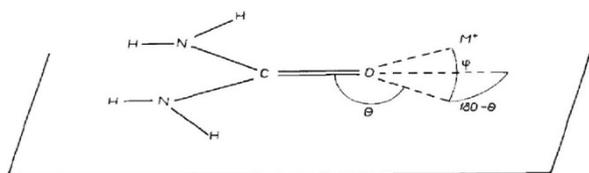


Fig. 3 Structure of urea.

Indeed, the urea forms a complex with the magnesium cation using the non-bonding electrons of the oxygen atom. Lebioda [18] has summarized the structural data known at that time for complexes of urea with metal ions, and his data confirm this consideration. The orientation of the urea molecules with reference to the metal ion is in the

direction of the oxygen electron pairs while in water it is in the direction of the dipole moment.

Complexes of urea with various magnesium salts are known. The crystal structures have been determined: nitrate [19], [20], chlorate [21], tetrafluoroborate [19], sulfate [22], [23], [32], chloride [19], bromide [24], [25], iodide [26], perrenate [27], formate [28] and dihydrogen phosphate [29].

Table 1 shows the known urea complexes of magnesium sulfate.

Complex numbers 1 and 3 are highly hygroscopic [31] and are not relevant for agrochemical use.

From the presented complexes, magnesium sulfate hexa urea hemi hydrate:  $MgSO_4 \cdot 6U \cdot \frac{1}{2} H_2O$  (2) has the highest potential for agrochemical use due to its high urea/magnesium sulfate ratio, low hygroscopicity and high stability. The structure of  $MgSO_4 \cdot 6U \cdot \frac{1}{2} H_2O$  is determined by monocrystalline X-ray structure analysis [23].

A number of magnesium salts also find their application in agrochemistry as a source of magnesium. These are the minerals: magnesite ( $MgCO_3$ ) and dolomite ( $CaCO_3 \cdot MgCO_3$ ), as well as magnesium nitrate. As a source of magnesium and sulphur, magnesium sulphate crystal hydrates are used. Most of these are minerals and are presented in Table 2.

The syntheses of urea complexes of magnesium salts can be reduced to two methodologies.

The first one is: Crystallization from solution under slow solvent evaporation. Typically, water is used as the solvent although the use of methanol as a solvent has been described [30].



The method is suitable for obtaining pure phases as well as single crystal patterns suitable for single crystal X-ray structure experiment.

Another method is the mechanochemical synthesis [33].



The method has many benefits. Easy and fast. No need for solvents, lots of energy and no waste products. It can be said that it is an "eco-friendly" process.

The main disadvantage is that it can only produce the complex with the highest stability. For  $MgSO_4$  and  $(H_2N)_2CO$ , this is  $MgSO_4 \cdot 6U \cdot \frac{1}{2} H_2O$ .

Here we describe a new method for the preparation of urea complexes of magnesium sulfate - solid-phase synthesis. The reaction is proceeded by grinding the crystal hydrate of magnesium sulfate (epsomite,  $MgSO_4 \cdot 7H_2O$ ) in the presence of urea in an agate mortar for several minutes, during which the reaction mixture is wetted by the water evolved during the interaction, forming a semi-liquid paste (Fig. 4).

TABLE 1 COMPLEXES OF MAGNESIUM SULFATE WITH UREA

<i>Nº</i>	<i>Complex</i>	<i>Notes</i>	<i>Source</i>
1	MgSO <sub>4</sub> .6U. 2H <sub>2</sub> O	Obtained from Yee in methanol	[30]
2	MgSO <sub>4</sub> .6U. 1/2 H <sub>2</sub> O	Slow evaporation, water	[23]
3	MgSO <sub>4</sub> .5U. 2H <sub>2</sub> O	Obtained from Yee in methanol	[30]
4	MgSO <sub>4</sub> .4U. H <sub>2</sub> O	Slow evaporation, water	[22]
5	MgSO <sub>4</sub> .U. 3H <sub>2</sub> O	Slow evaporation, water, 70°C	[32]
6	MgSO <sub>4</sub> .U. 2H <sub>2</sub> O	Slow evaporation, water	[32]

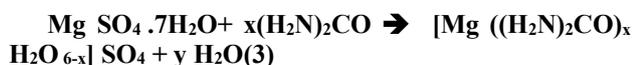
TABLE 2 MAGNESIUM SULFATE HYDRATE MINERALS FOUND ON EARTH AND MARS \*

<i>Hydrate</i>	<i>Mineral</i>	<i>Formula</i>
undecahydrate	Meridianiite*	MgSO <sub>4</sub> .11H <sub>2</sub> O
heptahydrate	Epsomite	MgSO <sub>4</sub> .7H <sub>2</sub> O
hexahydrate	Hexahydrite	MgSO <sub>4</sub> .6H <sub>2</sub> O
pentahydrate	Pentahydrite	MgSO <sub>4</sub> .5H <sub>2</sub> O
tetrahydrate	Starkeyite	MgSO <sub>4</sub> .4H <sub>2</sub> O
dihydrate	Sanderite	MgSO <sub>4</sub> .2H <sub>2</sub> O
monohydrate	Kieserite	MgSO <sub>4</sub> .H <sub>2</sub> O



Fig. 4 Type of the sample reaction before and after milling during solid phase synthesis of [Mg(H<sub>2</sub>O)((H<sub>2</sub>N)<sub>2</sub>CO)<sub>4</sub>(SO<sub>4</sub>)].

After that the sample is placed in a thermostat at 60°C to complete the interaction and to remove excess water.



$$X = 1, 4, 6$$

The products are characterized by infrared spectroscopy and powder X-ray phase analysis.

The recorded infrared spectra are presented in Figure 5. In the assignment of the absorption bands, the classical work of Nakamoto [34] was used, as well as published experimental and model data (Ab Initio Calculation) for similar complexes of magnesium salts with urea-iodide [26] and perrenate [27].

Powder diffractograms of [Mg(H<sub>2</sub>O)((H<sub>2</sub>N)<sub>2</sub>CO)<sub>4</sub>(SO<sub>4</sub>)] и [Mg ((H<sub>2</sub>N)<sub>2</sub>CO)<sub>6</sub>] SO<sub>4</sub> · 1/2 H<sub>2</sub>O are presented in Figures 6 and 7. Phase identification was carried out using the HighScore Plus program.

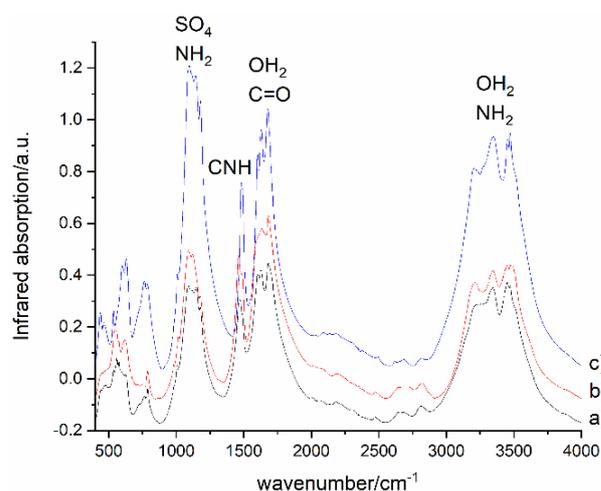


Fig. 5 IR spectra of reaction products:

- a) [Mg(H<sub>2</sub>O)((H<sub>2</sub>N)<sub>2</sub>CO)<sub>4</sub>(SO<sub>4</sub>)];
- b) [Mg ((H<sub>2</sub>N)<sub>2</sub>CO)<sub>6</sub>] SO<sub>4</sub> · 1/2 H<sub>2</sub>O;
- c) Mg(H<sub>2</sub>N)<sub>2</sub>CO( H<sub>2</sub>O)<sub>x</sub> SO<sub>4</sub>, (X=2;3).

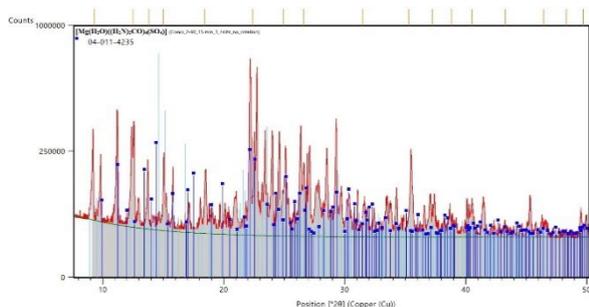


Fig. 6 Powder diffractograms of  $[\text{Mg}(\text{H}_2\text{O})((\text{H}_2\text{N})_2\text{CO})_6(\text{SO}_4)_6]$ , referred to (High Score 4.8) magnesium sulfate urea hydrate with reference code: 04-011-4235.

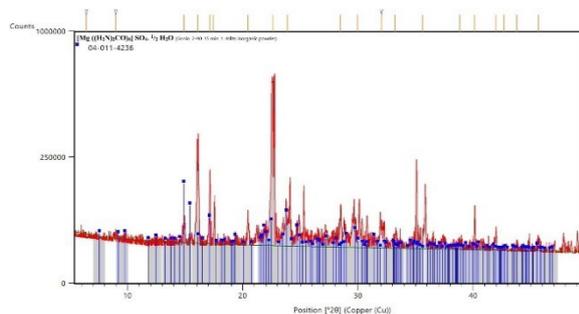


Fig. 7 Powder diffractograms of  $[\text{Mg}((\text{H}_2\text{N})_2\text{CO})_6] \text{SO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ , referred to (High Score 4.8) magnesium sulfate urea hydrate with reference code: 04-011-4236.

Data for the phases of  $\text{Mg}(\text{H}_2\text{N})_2\text{CO}(\text{H}_2\text{O})_x \text{SO}_4$ , ( $x=2;3$ ) are absent in the databases and therefore the generation of calculated diffraction patterns was performed for identification as well as relating the peaks of the experimental diffractogram to them. The result is presented in Figure 8.

The main product is  $[\text{Mg}(\text{H}_2\text{N})_2\text{CO}(\text{H}_2\text{O})_3] \text{SO}_4$  as is to be expected at a temperature of 60° C. By variation of the temperature, the pure phases  $[\text{Mg}(\text{H}_2\text{N})_2\text{CO}(\text{H}_2\text{O})_3] \text{SO}_4$  and  $[\text{Mg}(\text{H}_2\text{N})_2\text{CO}(\text{H}_2\text{O})_2] \text{SO}_4$  can be obtained [32].

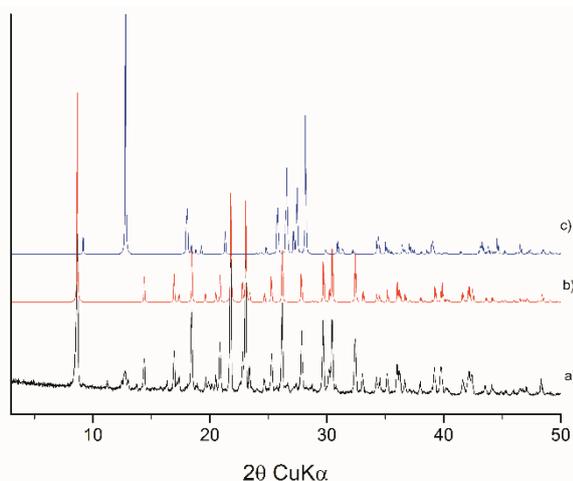


Fig. 8 PXRD diffractograms of  $\text{Mg}(\text{H}_2\text{N})_2\text{CO}(\text{H}_2\text{O})_x \text{SO}_4$  ( $x=2;3$ ):

- experiment;
- calculated  $[\text{Mg}(\text{H}_2\text{N})_2\text{CO}(\text{H}_2\text{O})_3] \text{SO}_4$ ;
- calculated  $[\text{Mg}(\text{H}_2\text{N})_2\text{CO}(\text{H}_2\text{O})_2] \text{SO}_4$ .

#### IV. CONCLUSIONS

The main problem in the application of bound nitrogen to soil is the losses associated with the formation of the volatile products and their evaporation into the atmosphere. Methods and developments to reduce these losses are described. A new highly effective method of reducing these losses is the use of urea complexes instead of pure urea. Urea complexes of magnesium sulphate used as fertiliser, in addition to nitrogen, introduce Mg and S into the soil – two bioelements commonly used in the composition of complex fertiliser applications. For this purpose, we are suggesting the use of magnesium sulphate hexaureate hemi hydrate –  $\text{MgSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ , which has a high urea/inorganic salt ratio in addition to good physicochemical properties. The developed solid-phase synthesis method, has the following advantages: no use of solvents, no side products, low energy consumption. It can be boldly stated that this is an "eco-friendly" process.

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