[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

Double Compounds of Urea with Magnesium Nitrate and Magnesium Sulfate

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In the course of an investigation of new fertilizer materials several new double compounds of urea with magnesium salts were obtained. Urea is quite hygroscopic at high humidities and also has the tendency to form double compounds. This tendency is sometimes a disadvantage in fertilizer mixtures, when urea displaces water of crystallization in forming a double compound with other constituents in the mixtures. Such a reaction has been attributed by Whittaker, Lundstrom and Hendricks[1] as the cause of stickiness encountered sometimes in fertilizer mixtures containing urea. The possibility was suggested that double compounds suitable for fertilizers might be obtained, which would be less hygroscopic than urea and also would not react further in mixtures to release free water from hydrated salts. A number of double compounds of urea are known, such as $Ca(NO_3)_2 \cdot 4CO(NH_2)_2$, $CaSO_4 \cdot 4CO(NH_2)_2$;[1] $SrBr_2 \cdot CO(NH_2)_2$,[2] etc.; and in some cases these render the urea in combination less hygroscopic.

The compound $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$ has been reported recently by Whittaker, Lundstrom and Shimp[3] of this Laboratory, in their study of the system magnesium sulfate–urea–water at 30°. This was formed from water solution while the sulfate compounds reported here were formed from alcoholic solution. In treating magnesium salts with urea in this manner three new double compounds were prepared and because of their high urea content, they were considered a potential source of nitrogen in fertilizers.

Preparation of New Double Compounds

The chemical compositions and the crystal properties of the new double compounds have been studied, but their physical condition and behavior in mixed fertilizer are still under investigation. One of these double compounds is a combination of urea and magnesium nitrate and the other two are of urea and sulfate in different proportions. They are represented by the formulas:

$$Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$$
$$MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$$
$$MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$$

Double Compound, $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$.—The nitrate double compound was prepared from equal parts (100 g. each) of the solids magnesium nitrate hexahydrate and urea by the following procedure. At first the crystalline nitrate and urea were mixed in small amounts in ratio of about 8 to 1 in a tube maintained at about 55°. After the appearance of a liquid phase, further amounts of the two salts were added slowly with gentle stirring in about the same proportion. When all the magnesium nitrate had been added, the resulting liquid was quite clear. The remainder of the urea was then introduced gradually. After removal of the tube from the bath, fine crystals came down with stirring and were separated from the mother liquor at room temperature. About 100 g. of the product was obtained from 100 g. each of magnesium nitrate hexahydrate and urea.

Larger individual crystals of this double compound for x-ray diffraction photographs were obtained by dissolving 30 g. of magnesium nitrate hexahydrate and 40 g. of urea in 30 cc. of ethyl alcohol at 40°. On standing at 20° well-formed crystals of $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$ were obtained.

Double Compound, $MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$.—This compound was obtained as individual orthorhombic crystals from methyl alcohol solution. One gram of powdered magnesium sulfate heptahydrate was dissolved in 20 cc. of methyl alcohol in a crystallizing dish (9 cm. in diameter). To this solution, 2.5 g. of finely powdered urea was added. On gently stirring the solution, or by slowly rotating the dish, the urea was dissolved completely. With the dish tightly covered to prevent evaporation of the alcohol, clear crystals of the compound formed on standing at 30°.

Double Compound, $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$.—This compound, when prepared from absolute methyl alcohol solution, formed polycrystalline masses with clear clusters of crystals. Clear, individual crystals, however, were prepared from 95% methyl alcohol solution. Two grams of powdered magnesium sulfate heptahydrate was dissolved in 25 cc. of 95% methyl alcohol in a crystallizing dish (9 cm. in diameter). To this was added 4 g. of powdered urea. On gently stirring the solution, or rotating the dish, the urea was dissolved completely. With the dish tightly covered, individual crystals formed on standing at room temperature, about 25°.

The similarity of conditions for formation of the two magnesium sulfate–urea compounds is quite striking, but the concentrations of solutions are different in the two cases. At the particular ratio of the salts used in preparing the six urea compound, individual crystals were obtained from 95% methyl alcohol, while polycrystalline masses only were obtained from absolute methyl alcohol.

Examination of the Compounds.—Chemical analyses were made and x-ray and optical properties were determined for the three compounds. The molecular weights of all three compounds, derived from the x-ray diffraction data, are in positive agreement with the values calculated from the chemical analyses. It is of interest to note that

(1) Whittaker, Lundstrom and Hendricks, *Ind. Eng. Chem.*, **25**, 1280 (1933).

(2) DeCarl, *Atti accad. Lincei*, **16**, 747 (1932).

(3) Whittaker, Lundstrom and Shimp, THIS JOURNAL, **58**, 1975 (1936).

the densities obtained for $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$ and $MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$ are identical within the limits of experimental error. Analyses for urea by the Yee and Davis urease method[4] and for magnesium by the magnesium ammonium phosphate method gave results checking consistently with calculated values for the three compounds. Some of the results are shown in Table I.

TABLE I

COMPOSITION OF THE DOUBLE COMPOUNDS OF UREA

Double compounds		$Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$	$MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$	$MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$
Mol. wt.	Calcd.	424.56	456.65	516.69
	Obsd.[a]	422.0	457.75	514.00
Urea, %	Calcd.	56.56	65.75	69.73
	Found	56.32	65.69	69.86
Mg, %	Calcd.	5.73	5.33	4.71
	Found	5.72	5.37	4.79
Total N calcd.		32.99[b]	30.68	32.53

[a] From measurements of the lattice constants by means of x-ray diffraction

$$\frac{\text{Mol. wt.}}{\text{Density}} = \frac{a \times b \times c \times \cos\beta \times \text{Avogadro's number}}{\text{No. of formula weights in the unit}}$$

[b] 26.4% urea nitrogen and 6.6% nitrate nitrogen.

Optical and x-Ray Examination.—Results of x-ray and optical measurements on the various salts are listed in Table II. Refractive index values are useful both for identification and for structure analysis. Measurements of the lattice constants combined with the density leads directly to the molecular weight, as listed in Table I, and thus to a check on the analytical data.

TABLE II

OPTICAL AND X-RAY DIFFRACTION DATA FROM SOME DOUBLE UREA COMPOUNDS WITH MAGNESIUM SALTS

Compounds		$Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$	$MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$	$MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$
Crystal symmetry and common forms		Monoclinic prismatic, (011), (010), (110)	Rhombic dipyramidal (101), (111)	(110), (111)
Space group		$C_{2h}^5 - P2_1/n$	$D_{2h}^{16} - Pnma$	$D_{2h}^{10} - Pccn$
Lattice dimensions, Å.	a	6.38	17.32	16.20
	b	18.10	11.40	19.97
	c	7.55	9.61	14.38
β		93°20′		
Form. wts. in unit		2	4	8
Refractive indices	α	1.393	1.515	1.493
	β	1.539	1.533	1.508
	γ	1.595	1.551	1.520
Density		1.596	1.596	1.458

(4) Yee and Davis, *Ind. Eng. Chem., Anal. Ed.*, **7**, 259 (1935).

Refractive indices were measured by the immersion method. x-Ray powder diffraction photographs, rotating crystal and equatorial zone Weissenberg photographs, about the crystallographic axes, were obtained for the three compounds; CuK radiation being used. Densities were determined by the Retger suspension method. None of the compounds is piezoelectric.

Since there are only two $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$ in the monoclinic prismatic unit of structure, it follows that the magnesium atoms must be in unique positions. In the space group $P2_1/n$ they are at symmetry centers about which the urea and water molecules are repeated. It thus is probable that the four oxygen ends of the urea molecules and the two water molecules are grouped around magnesium at the corners of an octahedron, giving magnesium a coördination number of six. The plane of the optic axes is (010) with the acute bisectrix 50° from the a axis and the low value of α suggests that the direction of vibration is approximately normal both to the planes of the nitrate and urea group, which planes would thus be parallel.

The space group of $MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$ requires the sulfate groups to be on symmetry planes which also contain one and possibly three urea molecules. It cannot be said whether $5CO(NH_2)_2$ and $2H_2O$ have their oxygen ends toward Mg or whether only $4CO(NH_2)_2 \cdot 2H_2O$ are so arranged. The birefringence of this compound is very low compared with that of the nitrate. This is also true of $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$, which in addition must have a very complex structure as indicated by the large number of formula weights in the unit.

The authors wish to express their thanks to M. E. Jefferson of this Laboratory for making the refractive index measurements.

Summary

Three new double compounds of urea with magnesium salts have been prepared, and the methods of preparation described.

Two of the compounds are with magnesium sulfate and one with magnesium nitrate. Their compositions are represented by the formulas $MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$, $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$ and $Mg(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot 2H_2O$; and they contain 65.7, 69.7 and 56.5% of urea, respectively. The first two contain more urea than any of the previously known double salts.

x-Ray and optical examinations have been made of the compounds and the properties have been given. From x-ray diffraction data the molecular weights of the compounds have been calculated and found to agree closely with those derived from the chemical analyses.

Their physical properties and behavior when mixed in fertilizers have not yet been determined.

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