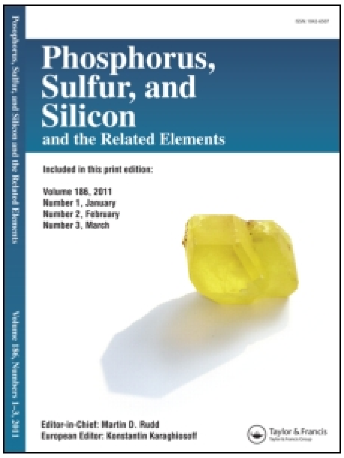

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A Novel Copper Ammonium Diphosphate--Dimorphic Cu 3 (NH 4) 2 (P 2 O 7) 2 ·3H 2 O

Albinas Pigaga[a]; Remigijus Juškėnas[a]; Algis Selskis[a]
[a] Institute of Chemistry, Vilnius, Lithuania

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A NOVEL COPPER AMMONIUM DIPHOSPHATE—DIMORPHIC $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$

Albinas Pigaga, Remigijus Juškėnas, and Algis Selskis
Institute of Chemistry, Vilnius, Lithuania

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This article deals with the insoluble compounds, formed in $CuSO_4$–$(NH_4)_4P_2O_7$–H_2O system. The solutions were analyzed by means of chemical analysis, the precipitate—by means of x-ray diffraction, chemical and thermal analysis, and FTIR spectroscopy. We have established that at least three poorly soluble compounds can form in the system $CuSO_4$–$(NH_4)_4P_2O_7$–H_2O. Their chemical formulae are $Cu_2P_2O_7 \cdot 5H_2O$ and polymorphic $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$. The first modification is most stable when $|Cu + P_2O_7| = 0.25$ M (n = 1.0), and, in a matter of days, Dimorph A transforms to Dimorph B, which has not been described in any publications.

Keywords: Chemical composition; copper; diphosphate; FTIR spectroscopy; XRD analysis

INTRODUCTION

Most metal ions form various poorly soluble and complex diphosphates. Two main factors affect the chemical composition of such compounds, namely the molar ratio of diphosphate ions to metal ions (n) and pH. Brown et al. in their classical work[1] showed, that some of the diphosphates are metastable. Akbaev investigated the $Cu_2P_2O_7$–$(NH_4)_4P_2O_7$–H_2O system, and described the formation of a compound corresponding to formula $2.5Cu_2P_2O_7 \cdot (NH_4)_4P_2O_7 \cdot 17H_2O$.[2] Suleimanova and Mukhamedzhanov investigated the $CuSO_4$–$(NH_4)_4P_2O_7$–H_2O system by the method of isomolar series.[3] They worked with 0.05 M solutions, and showed the composition of the precipitate to be $CuNH_4HP_2O_7 \cdot nH_2O$ by means of potentiometrical titration,

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Address correspondence to Albinas Pigaga, Institute of Chemistry, A. Goštauto 9, 2600 Vilnius, Lithuania. E-mail: viliuip@takas.lt or juskenas@ktl.mii.lt

electroconductivity, density and viscosity of the solutions. However, Suleimanova and Mukhamedzhanov indicated neither *n*, nor pH of the solutions they used, and the overall study does not appear to be trustworthy. Kopilevich et al. performed a contemporary investigation when $n = 0.05 \div 2.5$. They worked with 0.5 N $CuSO_4$ solution, however, they did not indicate the concentration of $(NH_4)_4P_2O_7$.[4,5] In the cases, when $n = 0.05–0.335$, $Cu_2P_2O_7 \cdot 5H_2O$ precipitates, and when $n = 0.67–1.0$, monoclinic $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$ precipitates. In the cases when $n =$ 0.5–0.6 the precipitate is a mixture of those two compounds.

RESULTS AND DISCUSSION

Kopilevich et al.[4] used only one copper concentration (0.5 N) and allowed as little as 4 h for the reaction to proceed. We decided to investigate the system used in (**3**) first. The solutions of 0.05 M $CuSO_4$ and 0.05 M $(NH_4)_4P_2O_7$ were mixed in isomolar series at ratios $n = 0.2$, 0.4, 0.5, 0.6, 0.7, 0.75, 0.8, 0.9, 1.0, 1.3, 1.5, and 2.0 and were filtered after 4 days. The dependence of residual concentrations *c* Cu, *c* NH_4 and *c* P_2O_7 on *n* is presented in Figure 1. The results are quite similar to those described in.[4] When $n = 0.2–0.6$ residual *c* NH_4 is nearly the same as in the initial mixture of solutions. When $n \geq 0.7$ residual *c* NH_4 is much lower, because some NH_4 is precipitated. *c* Cu reaches its minimum when $n = 0.75$. As it should be expected, XRD analysis showed, that at the molar ratios $n = 0.2–0.6$ the precipitate is composed of $Cu_2P_2O_7 \cdot 5H_2O$ only. On the other hand, when *n* grows as high as $n = 0.75–2.0$ we have observed the peaks of a monoclinic compound

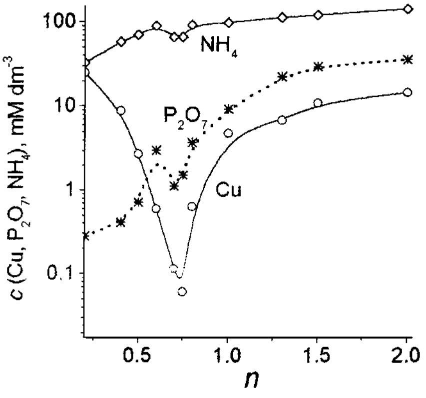

FIGURE 1 Dependence of residual concentrations *c* Cu, *c* P_2O_7, and c NH_4 on *n* after 96 h of interaction $|Cu + P_2O_7| = 0.05$ M.

which does not correspond to any already known chemical substance.[7] When $n = 0.7$, the mixture of both compounds forms according to XRD analysis. Then we determined the composition of the precipitate which was formed during the reactions with $n = 0.8$, 1.0 and 1.5. The molar ratios of copper, ammonia, pyrophosphate, and water (calculated by subtraction) are given below:

$n = 0.8$; $Cu : NH_4 : P_2O_7 : H_2O = 1.00 : 0.69 : 0.67 : 1.05$
$n = 1.0$; $Cu : NH_4 : P_2O_7 : H_2O = 1.00 : 0.65 : 0.66 : 1.08$
$n = 1.5$; $Cu : NH_4 : P_2O_7 : H_2O = 1.00 : 0.67 : 0.67 : 1.01$

These results, obtained by chemical and XRD analysis, point to the fact that at $n \geq 0.75$ $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$ forms, thus, this compound has polymorphic properties. One form is described in[4,5] we named it Dimorph A, and the other form is described here (we arbitrarily named it Dimorph B). Their XRD data are presented in Table I.

In the next series of experiments we investigated the influence of pH on the composition of precipitates by adding H_2SO_4 to pH 2.0, 3.0, 4.0, and NH_4OH to pH 7.0 to equimolar mixture $|Cu + P_2O_7| = 0.05$. At pH 8 no formation of precipitate was observed. XRD analysis showed, that at pH 3 the precipitate is composed of $Cu_2P_2O_7 \cdot 5H_2O$ only, at pH 5-7 it is composed of Dimorph B only, and at pH 4—it is a mixture of $Cu_2P_2O_7 \cdot 5H_2O$ and Dimorph B. These results suggest, that at the initial stages of precipitate formation, Dimorph A forms, which slowly changes to Dimorph B. Then we tried to determine the regularities of the transformation. For this purpose further experiments were performed with solutions having the following total copper and diphosphate concentrations $|Cu + P_2O_7| = 0.05$, 0.15, 0.25, 0.5, and 1.0 M ($n = 1.0$). Every day we took a sample from the suspension, filtered it and carefully washed the pellet. XRD analysis showed, that Dimorph A forms first, subsequently the precipitate contains both Dimorph A and Dimorph B, and finally, the only component of the precipitate left is Dimorph B. Time required for Dimorph A → Dimorph B transition depends on $|Cu + P_2O_7|$ ($n = 1$) as presented in Table II. As can be seen, Dimorph A is most stable at $|Cu + P_2O_7| = 0.25$ M, and least stable in the diluted solutions, when $|Cu + P_2O_7| = 0.05$ M. In the latter case, after 24 h we were able to detect only traces of Dimorph A.

There are slight differences between our and Kopilevich et al.[4,5] IR spectra of Dimorph A (Table III). The possible reason for that could be the different duration of the reaction. Dimorph A and Dimorph B IR spectra are significantly different (Table III). In the case of Dimorph A there is only one bond corresponding to the deformation vibration of NH_4^+ at 1444 cm^{-1}. In the case of Dimorph B the bond is split into two

TABLE I XRD Patterns of $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$

Dimorph A				Dimorph B	
Kopilevich et al.[4] results		Our results			
d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
8.749	100	8.918	100	9.422	32
6.129	7	6.188	21	6.180	76
5.468	14	5.528	32	5.617	43
		5.012	9	5.305	36
		4.735	23	5.017	100
4.374	14	4.400	18	4.628	30
3.898	6	3.946	13	3.853	7
3.633	7	3.652	30	3.704	3
		3.586	14	3.633	7
3.414	12	3.447	31	3.444	19
		3.365	31	3.343	2
3.296	24	3.310	50	3.233	5
3.074	38	3.084	38	3.071	47
2.813	21	2.854	13	2.983	5
				2.923	8
				2.891	51
				2.868	48
2.781	13	2.789	13	2.802	26
2.738	18	2.749	27	2.759	11
2.678	22	2.692	9	2.725	7
2.637	16	2.649	15	2.653	11
2.557	16	2.573	26	2.637	11
2.478	17	2.487	11	2.534	5
2.412	5	2.414	11	2.503	2
2.293	8	2.309	13	2.407	18
2.240	10	2.205	14	2.340	16
				2.311	8
2.196	9	2.160	3	2.242	3
				2.199	4
				2.171	3

TABLE II Dependence of Dimorph A → Dimorph B Transition Time on $|Cu + P_2O_7|$, $n = 1$

$\lvert Cu + P_2O_7 \rvert$, M	0.05	0.15	0.25	0.5	1.0
τ, days	1	3	8–10	4–5	3

τ is the time required for both Dimorph A and Dimorph B peeks to become visible in diffractograms.

TABLE III Vibration Frequencies of $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$

ν, (cm^{-1})			
Dimorph A (Kopilevich et al.[4,5] results)	Dimorph A (our results)	Dimorph B	Assignment
1670 sh	1690 w	1683 m	δH_2O
1640 m	1674 sh		
1430 s	1444 s	1440 s	δNH_4^+
		1411 m	
1120 s	1150 s	1127 s	νPO_3
1100 s	1131 s	1083 s	
	1116 s		
1050 s	1068 m		
1020 s	1035 s	1034 m	
990 s	1001 w		
910 s	916 sh	960 s	ν_{as}P—O—P
885 s	901 s		
730 s	749 m	769 m	ν_sP—O—P
660 sh	672 w	664 w	γPOH?
620 sh	633 w	607 sh	δPO_3
570 s	589 s	590 m	
550 s	564 s	541 m	

Sh: shoulder, s: strong, m: medium, w: weak.

components at 1440 and 1411 cm^{-1}, what is indicative of the loss of the tetrahedron symmetry of NH_4^+ ion.

In the case of Dimorph A there are two bonds at 1690 and 1674 (sh) cm^{-1} corresponding to the deformation vibrations of crystal water. Therefore, there are two different types of crystal water molecules in Dimorph A. In the case of Dimorph B there is only one bond at 1683 cm^{-1}, which indicates that there is one type of strongly deformed water molecules. There are six distinct bonds corresponding to vibrations of P—O bonds of terminal PO_3 moiety of diphosphate group in the case of Dimorph A: 1150, 1131, 1116, 1068, 1037, 1001 cm^{-1}. In the case of Dimorph B there are only three bonds, namely, 1127, 1083, 1034 cm^{-1} which suggests, that the P—O—P angle is much closer to 180° in Dimorph B than in Dimorph A.

Bonds corresponding to ν_{as}P—O—P and ν_sP—O—P are shifted to shorter wavelength in Dimorph B as compared with Dimorph A (960 cm^{-1} instead of 901 and 916sh cm^{-1}; and 769 cm^{-1} instead of 749 cm^{-1} correspondingly) while bonds corresponding to δPO_3 (633 and 564 cm^{-1}) are shifted to longer wavelengths (607sh and 541 cm^{-1} correspondingly).

The data of thermal analyses are identical for Dimorphs A and B. Kopilevich et al. studied the products and mechanism of thermolysis of

Dimorph A.[5] It is to be supposed that they are approximately the same for Dimorph B as well.

EXPERIMENTAL

All experiments were carried out at 18 ± 2°C. Stock 1M $CuSO_4$ and 1M $(NH_4)_4P_2O_7$ solutions were diluted to the appropriate concentrations. The mixing of solutions in order to obtain appropriate n was performed by pouring both solutions at the same time into the beaker while continuously stirring with a magnetic stirrer. The solutions were stirred for at most 8 h per day, then left overnight without stirring (16 h). The solutions were filtered and the pH was measured. The concentrations of copper, ammonium, and phosphate were measured after standing and adjusting the pH to ~2 by adding H_2SO_4. The precipitates were rinsed several times and dried at 40°C to constant weight. Residual Cu and P concentrations in the solution were determined by emission spectroscopy using a direct current argon plasma emission spectrometer Beckman SpectraSpan VI. Standard solutions were prepared from monoelement stock solutions containing 1000 mg dm^{-3} Cu or P. The measurements were carried out using Cu 224.700 nm and P 253.565 nm spectral lines. Ammonium was determined by distillation with sodium hydroxide. X-ray diffraction (XRD) patterns of the precipitate were measured using Cu K_α radiation selected by a secondary graphite monochromator. A continuous scan mode was used in the range of $5^\circ \leq 2\Theta \leq 60^\circ$ with a scan rate of 1° 2Θ min^{-1}. Infrared spectra were obtained with a FTIR spectrometer (Hartmann & Braun, Canada). The spectra were recorded in the range 2000–500 cm^{-1} using KBr discs.

Thermal analyses (thermogravimetry, differential thermogravimetry, and differential scanning calorimetry) were performed in air with Paulik–Paulik–Erdey module Q-1500D at a heating rate of 10°C min^{-1} up to 1000°C.

$Cu_2P_2O_7 \cdot 5H_2O$ was synthesized as described in Kokhanovskii and Zemcova,[6] $n = 0.4$.

$Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$ was synthesized as described in Kopilevich et al.,[4] $n = 1.0$, $|Cu + P_2O_7| = 0.25$, the solution was allowed to settle for 24 h. The actual way of preparation, described in Kopilevich et al.[4] recommended to allow the solution to settle for 4 h. However, our XRD analysis of precipitates showed, that 4 h were not enough to reach the equilibrium state. Twenty-four hours are supposed to be enough because the results of XRD analysis after 24 h are identical to those obtained after 2 or 6 days. Approximately 0.1 g of precipitate was accurately weighted and dissolved in 50 cm^3 0.7 M H_2SO_4. Concentrations of Cu and P were determined by emission spectroscopy. Ammonium was determined by distillation with sodium hydroxide from another part of the precipitate.

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