A novel copper potassium diphosphate – dimorphic $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$

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The article deals with the barely soluble compounds formed in the $CuSO_4$–$K_4P_2O_7$–H_2O system. The precipitates were analysed by X-ray diffraction, chemical analysis and FTIR spectroscopy. It has been established that at least three poorly soluble compounds can form in the system. Their chemical formulae are $Cu_2P_2O_7 \cdot 5H_2O$ and $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (two polymorphs). A known form of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*) or $Cu_2P_2O_7 \cdot 5H_2O$ transforms into a novel *Dimorph B* which has a different structure and has not been described in any previous publication. The vibration spectra point to a bent P–O–P bridge angle for all of these compounds. The values of this angle for copper–potassium and copper–ammonium salts as well as for $Cu_2P_2O_7 \cdot 5H_2O$ were estimated using Lazarev's relationship and the plot given by Rulmont et al.

Key words: copper, diphosphate, XRD analysis, FTIR spectroscopy, polymorphism

INTRODUCTION

Various diphosphates are in most common use as fertilizers, food additives, catalysts, electrode materials for batteries, and in metal finishing processes, chemical analysis, in production of fluorescent lamps, scintillators, piezoelectrics, ceramics, etc. Diphosphates also play one of the central roles in the chemistry of living cells. They have been extensively investigated for both practical and fundamental purposes, and there are a lot of publications dealing with the subject [1–4].

$P_2O_7^{4-}$ ions consist of two corner sharing PO_4 tetrahedra. Diphosphates form a variety of diverse compounds because of their ability to form a whole range of acidic and neutral, single and double salts, and crystallohydrates with a varying water content. For example, over 30 different Ca diphosphates have been synthesized [5–7]. A possible reason for this diversity is the lability of the P–O–P angle, resulting in a different relative spatial orientation of the two PO_4 tetrahedra. The values of P–O–P angles vary between 123 and 157°, except rare cases when this angle is 180°. The $P_2O_7^{4-}$ ion can have two borderline conformations: "eclipsed" (*cis*) and "staggered" (*trans*), but in most compounds $P_2O_7^{4-}$ shows an intermediate conformation [8, 9]. Some of the

diphosphates are metastable because of polymorphic modifications and / or variations in the crystal water content. We have established that $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$, which is formed in the $CuSO_4$–$(NH_4)_4P_2O_7$–H_2O system, transforms into another polymorphic modification in a matter of hours or days [10]. It is interesting that this other modification (according to XRD data and IR spectra) forms in a thermal reaction between CuO and $NH_4H_2PO_4$ at 220–300 °C [11, 12]. We expected that in the $CuSO_4$–$K_4P_2O_7$–H_2O system a similar polymorphic transformation of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ would be possible. While copper diphosphate containing solutions are used in electroplating [13, 14], the precipitation regularities of copper diphosphates are not well established. There is only one paper dealing with the $Cu(NO_3)_2$–$K_4P_2O_7$–H_2O system, know to us [15]. The authors have investigated the formation of the precipitate at different molar ratios of diphosphate ions to metal ions (*n*), using 0.5 M solutions. If *n* is below 0.54, $Cu_2P_2O_7 \cdot 5H_2O$ precipitates. If *n* = 0.74–1.86, $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ precipitates. For values of *n* between 0.6 and 0.67, a mixture of the two compounds is formed. For *n* > 1.86, the solution remains clear and no precipitate is formed. The publication also presents X-ray diffractograms and IR data, but no XRD patterns. In the present paper, we report the results of our detailed investigations of the novel dimorph of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$.

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EXPERIMENTAL

All experiments were carried out at 18 ± 2 °C. Stock 1 M $CuSO_4$ and 1 M $K_4P_2O_7$ solutions were diluted to the appropriate concentrations. The mixing of the solutions was performed by pouring both solutions at the same time into a beaker while continuously stirring with a magnetic stirrer. The necessary pH was immediately adjusted using concentrated and diluted (1 M and 0.1 M) H_2SO_4. Because the pH of the mixture increased slowly during the first 2–3 hours of mixing, it was corrected once every 20 min. For reaction times longer than 3 days, the reaction mixture was poured into a conical flask and heat-sealed with a polished glass plug and paraffin to prevent evaporation. The suspensions were filtered using a *Filtrak* filter, "a slow filtering for finest deposits", a Buchner funnel and a vacuum-jet pump.

The precipitates were washed several times and dried in the air to a constant weight. Approximately 0.1 g of the precipitate was accurately weighed and dissolved in 20 cm³ of 5% HNO_3.

Cu^{2+} and K^+ concentrations in the solutions were determined by atomic absorption spectrometry using a Perkin–Elmer AAS-603 spectrophotometer with the acetylene-air flame. Standard solutions were prepared from monoelement stock solutions containing 1000 mg/l of Cu^{2+} and K^+. The measurements were carried out using Cu 324.9 nm and K 383.6 nm spectral lines.

The quantities of $P_2O_7^{4-}$ were detected as PO_4^{3-} photometrically with ammonium molybdate after dissolving and hydrolysing the precipitates in 5 M H_2SO_4.

X-ray diffraction (XRD) patterns of the precipitates were measured using Cu K_α radiation selected by a secondary graphite monochromator. A continuous scan mode was used in the range of $5° \leq 2\theta \leq 45°$ with a scan rate of 1° min⁻¹.

The infrared spectra were obtained with a FTIR Hartmann & Braun spectrometer in the region of 4000 to 500 cm⁻¹ as KBr pellets.

$Cu_2P_2O_7 \cdot 5H_2O$ was synthesized as described in reference [15], $n = 0.4$.

$Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ was synthesized as described in reference [15], $n = 1.0$.

The P–O–P angle values were estimated using Lazarev's relationship [16]:

$$\Delta = (\nu_{as}\text{P–O–P} - \nu_s\text{P–O–P}) / (\nu_{as}\text{P–O–P} + \nu_s\text{P–O–P}) = f(\alpha)$$

and the plot given by Rulmont et al. [17, 18].

RESULTS AND DISCUSSION

The formation of poorly soluble compounds at Cu^{2+} and $P_2O_7^{4-}$ concentrations 0.05 M in the pH range from 4.0 to 6.0 was investigated. The effect of excess $P_2O_7^{4-}$ at constant $[Cu^{2+}] = 0.05$ M (pH 5.0) was also studied with n values 1.25, 1.5 and 1.75. According to XRD data, under all the conditions tested, the formation of poorly soluble compounds occurs in the following steps: semiamorphous voluminous precipitate $\rightarrow Cu_2P_2O_7 \cdot 5H_2O \rightarrow$ known $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O \rightarrow$ a new compound not described in any previous publication, with the following exception: at pH 4 the formation of known $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ was not observed. Apparently, at a low pH, $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ converts to a new compound at a high rate, making its detection in diffractograms impossible. A detailed description of the precipitate formation process in the $CuSO_4$–$K_4P_2O_7$–H_2O system will be presented in a further publication. In this paper, we report the properties of the new compound.

Four of the precipitates that in the diffractograms contained only peeks corresponding to the new compound were analysed (Table 1). In all four cases, the formula of the compound corresponded to $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$. These results indicate that $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ has polymorphic properties. One form is described in reference [15] (*Dimorph A*), and the other form is described here (*Dimorph B*).
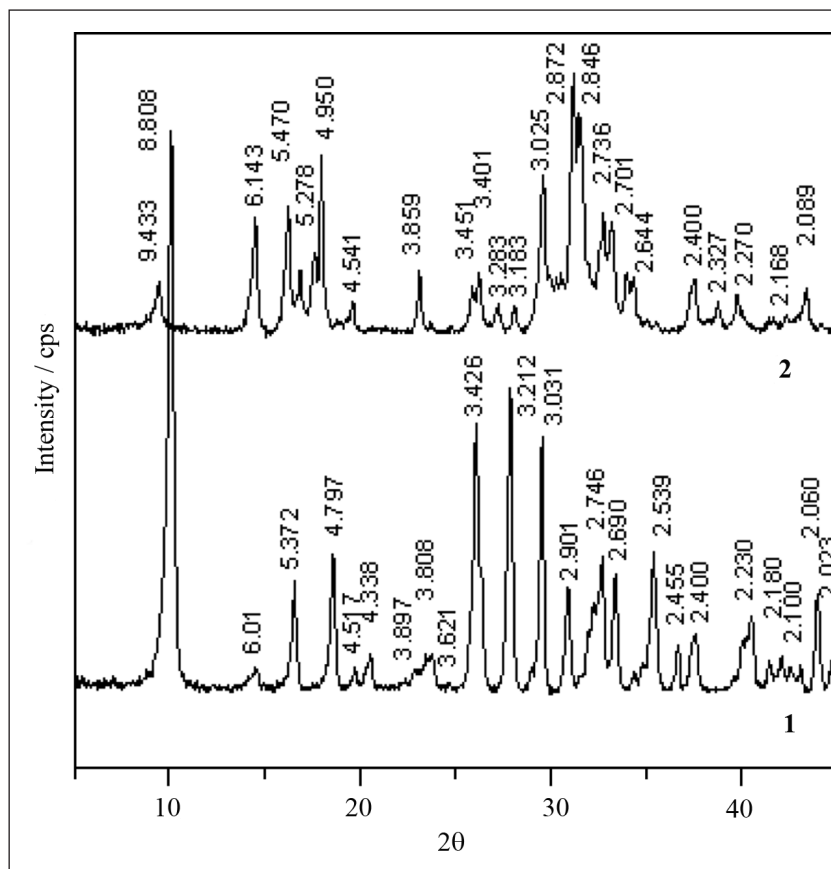

Fig. 1. X-ray diffractograms: *1* – $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph A*), *2* – $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ (*Dimorph B*)

Their XRD data are presented in Table 2 and the diffractograms in Fig. 1. Analysis of the data show that the new *Dimorph B* crystallizes in the same monoclinic system as does *Dimorph A*.

Table 1. **Molar ratios of copper, potassium, diphosphate and water (calculated by subtraction) for precipitates determined by chemical analysis**

pH	n	Duration of mixing, days	$Cu : K : P_2O_7 : H_2O$
4.0	1.0	30	1.00 : 0.68 : 0.67 : 1.03
5.0	1.0	15	1.00 : 0.68 : 0.66 : 1.00
5.5	1.0	10	1.00 : 0.67 : 0.68 : 1.02
5.0	1.5	10	1.00 : 0.66 : 0.67 : 0.99

The time required for the formation of *Dimorph B* distinctly depends on pH and n (Table 3). The varied duration the transition *Dimorph A → Dimorph B* process takes under the same conditions can be explained by the stochastic nature of its initiation and progression in an autocatalytic reaction manner. Indeed, if the reaction mixture is seeded with a small amount of *Dimorph B*, the transition occurs much faster.

The formation of *Dimorph B* was investigated. Every day a sample of the suspension was taken, filtered and carefully washed. After 30 days, samples were taken every 5 days. The transition time (τ) is shortest when pH is 5.5, and the rise of pH to 6.0 drastically increases τ (approximately ten times).

Table 2. **XRD patterns of $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ and $Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$ *Dimorph B* ([6] results)**

$Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$				$Cu_3(NH_4)_2(P_2O_7)_2 \cdot 3H_2O$	
Dimorph A		Dimorph B		Dimorph B	
d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
8.808	100	9.433	18	9.422	32
6.01	3	6.143	44	6.180	76
5.372	19	5.47	51	5.617	43
		5.278	27	5.305	36
		5.053	35	5.017	100
4.797	24	4.95	73		
4.517	3	4.541	14	4.628	30
4.338	6				
3.897	2	3.859	23	3.853	7
3.808	5	3.76	3	3.704	3
3.752	5				
3.621	1	3.595	2	3.633	7
3.426	48	3.451	17	3.444	19
		3.401	22	3.343	2
3.212	55	3.283	10	3.233	5
3.088	4	3.183	10		
3.031	46	3.025	61	3.071	47
		2.981	23	2.983	5
		2.955	22	2.923	8
2.901	18	2.932	23	2.891	51
		2.872	100	2.868	48
2.84	2	2.846	86	2.802	26
2.808	10				
2.783	15				
2.746	24	2.736	47	2.759	11
2.69	20	2.701	43	2.725	7
		2.644	23	2.653	11
2.614	3	2.617	21	2.637	11
2.582	4	2.566	5	2.534	5
2.539	25	2.529	4	2.503	2
2.455	8	2.475	1		
2.4	10	2.4	19	2.407	18
2.28	2			2.340	16
2.257	9	2.327	10	2.311	8
2.243	10	2.27	13	2.242	3
2.23	13	2.184	5	2.199	4
2.18	4	2.168	5	2.171	3

Table 3. Dependence of *Dimorph B* transition time (τ) on pH and *n* at [Cu^{2+}] = 0.05 M, pH 5.0

pH	*n*	τ, days
4.0	1.0	14–18, 17–24, 22–27
5.0	1.0	5, 6, 6–7, 7, 9–10, 11–13
5.5	1.0	3, 4–5, 6–7
6.0	1.0	50–65, 80–110
6.7	1.0	>150, >150
5.0	1.25	4, 4, 5, 7
5.0	1.5	3, 4, 4, 5
5.0	1.75	1, 1, 2, 2

Note. τ is the interaction time required for both *Dimorph* A (or Cu$_2$P$_2$O$_7 \cdot$ 5H$_2$O) and *Dimorph B* peeks to become visible in diffractograms.

The reduction of pH to 5.0 and 4.0 rises τ markedly (approximately two and four times, respectively). An increase of *n* from 1.0 to 1.75 at a constant [Cu^{2+}] = 0.05 M and pH 5.0 substantially reduces τ. Apparently, the increase in the unbound diphosphate ion concentration (at pH 5 the main form is H$_2$P$_2$O$_7{}^{2-}$) substantially accelerates the transition process. The moderate reproducibility shows that transition might be influenced by some uncontrolled or stochastic factors.

Analysis the IR spectra of *Dimorph A* and *Dimorph B* shows that the absorption bands are significantly different (Table 4, Fig. 2). There are seven distinct bands corresponding to P–O vibrations of the terminal PO$_3$ moiety of the diphosphate group in the case of *Dimorph A*: 1190, 1162, 1142, 1109, 1072, 1036, 1003 cm^{-1}. In the case of *Dimorph B*, there are only three bands at 1129, 1089 and 1036 cm^{-1}, suggesting, that the P–O–P angle is closer to 180° in *Dimorph B* than in *Dimorph A*.

Bands corresponding to ν_{as} P–O–P and ν_s P–O–P are shifted to shorter wavelengths in *Dimorph B* in comparison to *Dimorph A* (954 cm^{-1} instead of 918 and 889 cm^{-1}; and 774 cm^{-1} instead of 737 cm^{-1}, respectively).

The appearance of symmetric and antisymmetric bridge vibrations in the infrared spectra points to a bent P–O–P bridge configuration. No ν_s P–O–P vibrations are observed in the infrared spectrum when the bridge is linear.

Interestingly, the band corresponding to ν_{as} P–O–P for the copper–potassium *Dimorph A*, which is analogous to the copper–ammonium *Dimorph A* [10], is split into two components. This confirms the lower symmetry of the crystal cell in comparison to both (copper–ammonium and copper–potassium) *Dimorph B*, where appropriate single bands exist.
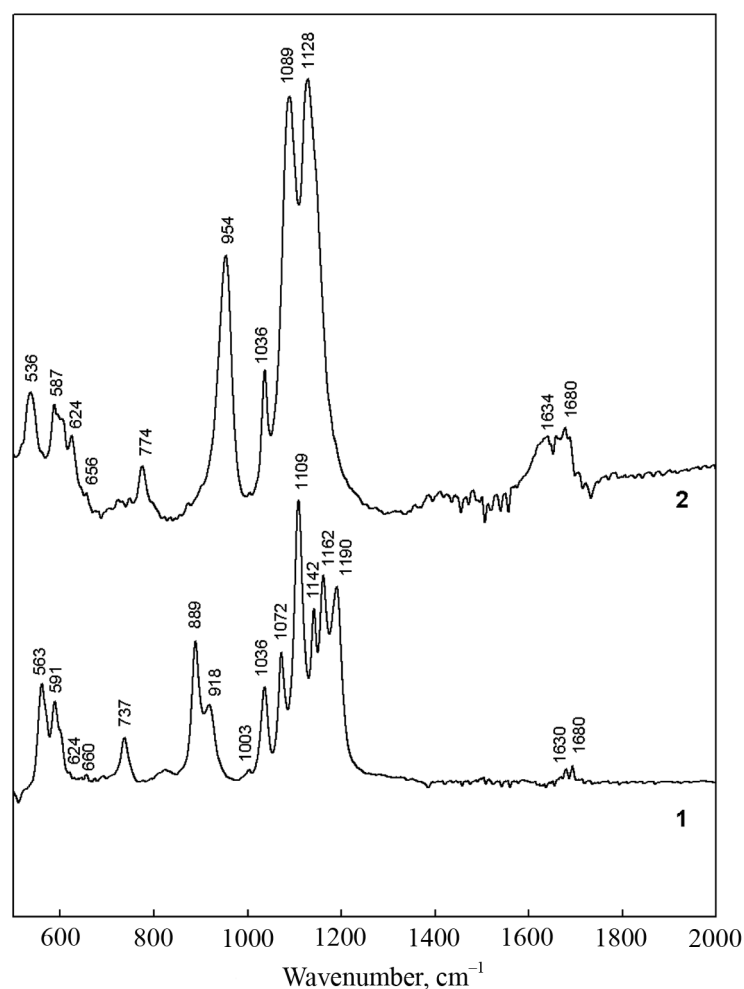

Fig. 2. FTIR spectra: *1* – Cu$_3$K$_2$(P$_2$O$_7$)$_2 \cdot$ 3H$_2$O (*Dimorph A*), *2* – Cu$_3$K$_2$(P$_2$O$_7$)$_2 \cdot$ 3H$_2$O (*Dimorph B*)

Table 4. Vibration frequencies of Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O and Cu$_3$(NH$_4$)$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O Dimorph B [6], (cm^{-1})

Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O		Cu$_3$(NH$_4$)$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O	Assignment
Dimorph A	*Dimorph B*	*Dimorph B*	
1670 w	1680 w	1683 m	δH$_2$O
1630 w	1634 w		
		1440 s	δNH$_4^+$
		1411 m	
1190 s	1128 s	1127 s	
1162 s	1089 s	1083 s	
1142 s	1037 m	1034 m	
1109 s			νPO$_3$
1072 m			
1036 m			
1003 w			
918 m	954 s	960 s	ν$_{as}$P–O–P
889 s			
737 s	774 m	769 m	ν$_s$P–O–P
660 sh	656 w	664 w	γPOH?
624 w	624 w	607 sh	
591 s	587 m	590 m	δPO$_3$
563 s	536 m	541 m	

Note: sh – shoulder, s – strong, m – medium, w – weak.

Table 5. The values of the P–O–P angle for Cu$_3$Kat$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (Kat = K, NH$_4$) and Cu$_2$P$_2$O$_7$ · 5H$_2$O

Compound	100 Δ	P–O–P angle value
Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (*Dimorph A*)	10.15	124.5
Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (*Dimorph B*)	10.34	125.1
Cu$_3$(NH$_4$)$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (*Dimorph A*)	9.87	123.1
Cu$_3$(NH$_4$)$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (*Dimorph B*)	10.67	126.2
Cu$_2$P$_2$O$_7$ · 5H$_2$O	10.88	127.1

The similarities between the XRD patterns and vibration spectra of the copper–ammonium and the copper–potassium *Dimorph B* imply that they are isostructural.

The values of the P–O–P angle were estimated using Lazarev's relationship for the copper–ammonium and copper–potassium dimorph pairs and for Cu$_2$P$_2$O$_7$ · 5H$_2$O (Table 5). All angles are relatively low and vary within a narrow range (123.1–127.1°). As a result of transformation of *Dimorph A* to *Dimorph B*, the P–O–P angle becomes slightly more obtuse. It should be noted, however, that while the IR absorption bands undergo a significant wavelength shift, the difference between ν$_{as}$ P–O–P and ν$_s$ P–O–P remains virtually the same, allowing a conclusion that all the P–O–P angles remain in a narrow range around 125° which lies at the lower end of the P–O–P angles observed in most diphosphates. Because such a small change in P–O–P angle cannot explain the dramatic shift of IR absorption bands, it must be due to some steric effects, obviously a different conformational orientation of the P$_2$O$_7^{4-}$ ion.

CONCLUSIONS

At least three poorly soluble compounds can be formed in the CuSO$_4$ – K$_4$P$_2$O$_7$ – H$_2$O system: a single salt Cu$_2$P$_2$O$_7$ · 5H$_2$O and two dimorphs Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O. A known form of Cu$_3$K$_2$(P$_2$O$_7$)$_2$ · 3H$_2$O (we called it *Dimorph A*) transforms into a new *Dimorph B* which has a different structure and has not been described in any previous publication.

The similarities between the XRD patterns and vibrations spectra of copper–ammonium and copper–potassium *Dimorph's B* imply that they are isostructural.

The vibration spectra indicate a bent P–O–P bridge angle for all of these compounds. The values of this angle for copper–potassium and copper–ammonium salts and Cu$_2$P$_2$O$_7$ · 5H$_2$O were estimated using Lazarev's relationship and the plot given by Rulmont et al. This angle is closer to 180° for *Dimorphs B* than for *Dimorphs A*. All angles are relatively small and vary in a narrow range (123.1–127.1°).

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NAUJAS VARIO KALIO DIFOSFATAS – $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$ DIMORFINĖ DRUSKA

S a n t r a u k a

Mažai tirpūs junginiai, susidarantys sistemoje $CuSO_4$–$K_4P_2O_7$–H_2O, buvo tirti rentgeno spindulių difrakcijos, FTIR spektrometrijos ir cheminės analizės metodais. Nustatyta, kad sistemoje susidaro paprastoji druska $Cu_2P_2O_7 \cdot 5H_2O$ ir dvi dimorfinės dvigubosios druskos $Cu_3K_2(P_2O_7)_2 \cdot 3H_2O$. Anksčiau mokslinėje literatūroje aprašyta dviguboji druska, sąlyginai pavadinta *Dimorfu A*, pereina į neaprašytą tokios pačios sudėties, bet kitokios struktūros junginį, sąlyginai pavadintą *Dimorfu B*. *Dimorfas A* reakcijos mišinyje žymiai stabilesnis, negu analogiška dimorfinė druska, susidaranti sistemoje $CuSO_4$–$(NH_4)_4P_2O_7$–H_2O.

IR vibraciniai spektrai rodo, kad P–O–P kampas yra netiesinis – lenktas. P–O–P kampas buvo nustatytas vario–kalio ir vario–amonio dimorfinėms druskoms bei paprastajai druskai $Cu_2P_2O_7 \cdot 5H_2O$, naudojant Lazarevo lygtį ir Rulmonto priklausomybę. Šie kampai yra palyginti maži ir kinta siaurame, 123,1–127,1°, intervale. *Dimorfų B* kampai yra didesni negu *Dimorfų A* kampai.