

Ethylenediammonium bis[Copper(II) Monohydrogendiphosphate Ethylenediamine] Trihydrate

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Received May 27, 1993; in revised form September 27, 1993; accepted October 4, 1993

Chemical preparation, calorimetric studies, crystal structure, and IR absorption spectra are given for a new metal-organic diphosphate. From a structural point of view the title compound $\text{Cu}_2(\text{C}_2\text{N}_2\text{H}_{10})(\text{HP}_2\text{O}_7)_2(\text{C}_2\text{N}_2\text{H}_8)_2 \cdot 3\text{H}_2\text{O}$ is an intricate stacking of copper(II) atoms, ethylenediammonium groups, $\text{HP}_2\text{O}_7^{4-}$ anions, and both ethylenediamine and water molecules. This layered arrangement has a monoclinic unit cell with $a = 18.808(8)$ Å, $b = 9.631(2)$ Å, $c = 14.019(8)$ Å, and $\beta = 109.63(5)^\circ$. The space group is $C2/c$ and $z = 4$. As in all atomic arrangements including acidic diphosphate groups one observes the formation of an infinite network of anions connected by strong H-bonds, infinite $(\text{HP}_2\text{O}_7)_n$ chains parallel to the b direction, for the present structure. The copper atom has a square-pyramidal fivefold coordination built by two nitrogen atoms, two oxygen atoms, and one water molecule. Another interesting feature of the title compound is the coexistence of both ethylenediammonium groups and ethylenediamine molecules in the atomic arrangement. A chelated complex of the formula $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)(\text{HP}_2\text{O}_7)(\text{H}_2\text{O})]^-$ is observed. © 1994 Academic Press, Inc.

I. INTRODUCTION

The present work is a contribution to two different types of systematic investigation. The first one is devoted to a general approach aimed at combining to an inorganic framework a polar organic cation through a chiral molecule, so as to induce a noncentric crystal structure. These materials, built up through van der Waals, ionic, and hydrogen bonding interactions, are often more resistant than similar purely organic polar materials. Crystals designed with this idea of chirality may be a new generation of materials with enhanced nonlinear quadratic properties (1). This approach must begin by systematic chemical

investigations in order to master, in a first step, the multiple parameters involved in chemical preparations.

The second field of investigation deals with the geometry of the infinite networks ("macroanions") built by acidic phosphoric anions. In all atomic arrangements including acidic phosphoric anions, condensed or not, these anions are connected by strong hydrogen bonds so as to build infinite networks with various geometries, chains, ribbons, layers, or 3D arrangements. In most cases the O-O distances in the H-bonds interconnecting these anionic entities are shorter than the O-O distances in the constituting PO_4 tetrahedra. Acidic anions are relatively rare in the field of condensed phosphates except in the diphosphate family where the occurrence of three different types of acidic groups, $\text{HP}_2\text{O}_7^{3-}$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$, and $\text{H}_3\text{P}_2\text{O}_7^-$, is common. The title compound provides a new example of such an association, since four infinite $(\text{HP}_2\text{O}_7)_n$ chains cross the unit cell.

In addition, the ethylenediammonium bis[copper(II) ethylenediamine monohydrogendiphosphate] trihydrate, $\text{Cu}_2(\text{C}_2\text{N}_2\text{H}_{10})(\text{HP}_2\text{O}_7)_2(\text{C}_2\text{N}_2\text{H}_8)_2 \cdot 3\text{H}_2\text{O}$ obtained during these investigations, but with a nonchiral organic molecule, reveals an interesting example of a transition metal complexed with unusual bidentate ligands, HP_2O_7 and ethylenediamine. Differential scanning calorimetric and IR absorption studies are added to the structural investigation.

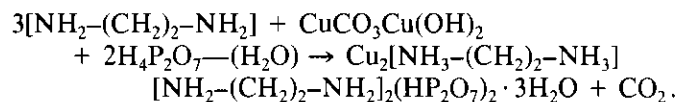
II. CRYSTAL CHEMISTRY

1. Chemical Preparation

As part of a systematic investigation of the $\text{H}_4\text{P}_2\text{O}_7\text{-M}^{\text{II}}\text{O}$ -ethylenediamine systems we previously characterized $(\text{C}_2\text{H}_{10}\text{N}_2)_2\text{P}_2\text{O}_7$ (2), $(\text{C}_2\text{H}_{10}\text{N}_2)_3(\text{HP}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (3), and $(\text{C}_2\text{H}_{10}\text{N}_2)\text{H}_2\text{P}_2\text{O}_7$ (4). During attempts to

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reproduce the preparation of Cu(C₂N₂H₁₀)P₂O₇ · H₂O (5) by neutralization of H₄P₂O₇ with copper hydroxycarbonate and ethylenediamine in a 1 : 1 : 1 mole ratio, an excess of the organic molecule was accidentally used. We observed, after evaporation of the obtained solution, the formation of dark blue multifaceted crystals. We were surprised by the difference, in color and shape, between these crystals and those of the previous Cu(C₂N₂H₁₀)P₂O₇ · H₂O compound which were pale blue regular monoclinic prisms. To determine the stoichiometry of this new compound, we analyzed phosphorous by UV absorption at 430 nm, copper by gravimetry, and protons by a volumetric method (6). Taking into account the approximate character of chemical analysis, the dark blue compound seems to have the formula Cu₂(C₂N₂H₁₀)(HP₂O₇)₂(C₂N₂H₈)₂ · 3H₂O, in which a part of the starting amount of ethylenediamine was not protonated. The present structural study will show that in the resulting compound this portion is in fact engaged in the formation of an adduct in which both ethylenediammonium groups and ethylenediamine molecules coexist. The chemical preparation, run at room temperature, is then successfully reproduced with a 3 : 2 : 2 mole ratio according to the reactional equation



The diphosphate acid is prepared by using a concentrated Na₄P₂O₇ solution and ion exchange resin "Amberlite IR 120." The copper(II) hydroxycarbonate used in the reaction is freshly synthesized from copper chloride and sodium carbonate. The organic molecule is a pure ethylenediamine (97%).

The obtained intense blue solution, evaporated at room temperature for several weeks, leads to intense blue short multifaceted monoclinic prisms. The compound is stable for months under normal conditions of temperature and hygrometry.

2. Crystallographic Features

The Weissenberg and oscillation photographs with Cu(*k*_{α1α2}) radiation show that the title compound crystallizes in the monoclinic system. The observed existence conditions derived from Weissenberg photographs

$$\begin{aligned} hkl \quad h+k &= 2n \\ h0l \quad l &= 2n(h=2n) \\ 0k0 \quad (k &= 2n) \end{aligned}$$

are consistent with *Cc* or *C2/c* space groups. The structural determination shows that the proper space group is the centrosymmetrical one with the unit-cell dimensions *a* = 18.732(3) Å, *b* = 9.596(1) Å, *c* = 13.959(2) Å, β = 109.50(1)° refined using a low scan-speed powder diffractogram.

The indexed powder diffractogram is reported in Table 1. The average density value, *D*_m = 2.03 g · cm⁻³, measured at room temperature using bromobenzene as pycnometric liquid is in agreement with the calculated *D*_x = 1.981 g · cm⁻³. The cell contains four formula units of the title compound.

3. Thermal Behavior

TGA and DSC were carried out on SETARAM TG70 and DSC92. TGA experiments were performed with a specimen of 140 mg in an open silica crucible and heated from 300 to 700 K at various rates in air. DSC analysis was carried out using 10-mg samples sealed in an aluminum DSC crucible; an empty aluminum crucible was used as reference and samples were heated from 293 to 543 K in air at various heating rates from 3 to 15 K/min.

Thermogravimetric analysis shows that dehydration occurs in one asymmetric step within the temperature range 420–531 K. The compound decomposes with maximum elimination of NH₃ at 580 K (Fig. 1a). On the DSC curve (Fig. 1b) a pronounced endothermic effect corresponding to the loss of the water molecules is observed between 426 and 485 K. The average dehydration enthalpy is Δ*H*_m = -121 KJ · mole⁻¹. By means of the DSC and the two nonisothermal Ozawa (7), and Kissinger (8) methods used chiefly for studying the decomposition of substances, we calculate the activation energy of dehydration, *E*_a = 36 KJ · mole⁻¹.

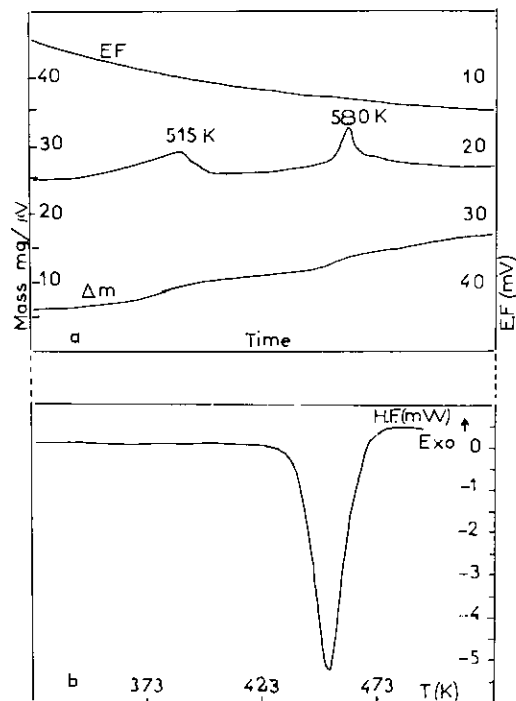


FIG. 1. Thermal analysis of Cu₂(C₂N₂H₁₀)(HP₂O₇)₂(C₂N₂H₈)₂ · 3H₂O. (a) TGA weight loss curve in air at heating rate of 20 K · min⁻¹; (b) DSC analysis in air at heating rate of 3 K · min⁻¹.

TABLE 1
Indexed Powder Diffractogram of $\text{Cu}_2(\text{C}_2\text{N}_2\text{H}_{10})(\text{HP}_2\text{O}_7)_2(\text{C}_2\text{N}_2\text{H}_8)_2 \cdot 3\text{H}_2\text{O}$

$h k l$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{obs.}}$	$h k l$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{obs.}}$
2 0 0	8.82	8.83	22	4 0 4	2.292	2.296	9
1 1 1	7.66	7.68	30	4 0 6		2.293	
1 1 1	6.63	6.63	36	1 3 4	2.207	2.209	5
2 0 2	6.38	6.40	23	8 0 0		2.207	
0 2 0	4.79	4.80	6	8 0 4	2.171	2.205	5
2 0 2	4.59	4.59	5	7 1 5		2.173	
4 0 2	4.41	4.41	30	5 1 6	2.147	2.168	9
3 1 1	4.30	4.30	12	5 3 4		2.168	
1 1 3	4.17	4.17	13	6 2 2	2.125	2.149	8
3 1 3	3.894	3.897	100	6 2 5		2.146	
1 1 3	3.657	3.660	3	2 4 2	2.105	2.126	6
2 0 4	3.482	3.487	10	2 4 3		2.126	
5 1 1		3.483		7	4 4 2	2.107	
0 0 4	3.290	3.290	7		0 4 3	2.037	2.105
4 2 0	3.248	3.249	27	8 2 2	2.104		
4 2 2		3.247		23	7 3 1	2.039	
4 0 2	3.200	3.204	23		5 1 4	2.013	2.037
3 1 4		3.200		5 1 2	2.033		
4 0 4	2.913	3.198	11	9 1 3	1.978	2.020	4
3 1 3		2.917		7 3 3		2.014	
1 1 4	2.912	2.912	11	8 2 0	1.858	2.005	3
3 3 1	2.839	2.843	8	2 0 6		1.979	
5 1 4	2.808	2.817	6	7 1 6	1.774	1.979	3
3 3 0		2.811		2 4 3		1.977	
1 3 2	2.773	2.776	6	6 4 0	1.774	1.860	3
3 3 1	2.660	2.663	10	6 4 3		1.859	
3 1 5		2.663		1 3 6	1.852		
4 2 4	2.506	2.661	11	1 3 5	1.697	1.773	3
6 2 0		2.509		0 4 5		1.773	
6 2 3	2.507	2.507	11	9 3 4	1.666	1.699	5
7 1 3	2.486	2.503	9	6 4 2		1.698	
1 1 3		2.488		6 0 8	1.697		
1 1 5	2.405	2.406	6	2 4 5	1.592	1.667	5
6 0 2		2.404		2 4 6		1.666	
0 4 0	2.314	2.399	5	5 3 7	1.592	1.666	5
2 0 6		2.317		6 4 3		1.595	
2 4 0	2.315	2.315	5	6 4 6	1.593	1.594	5
2 4 1	2.315	5 3 5	1.593				

It should be noted that the removal, by dehydration, of the water molecules from the structure leads to the anhydrous compound with persistent blue color until 580 K. Thus, the elimination of H_2O (515 K) preceding the Cu-NH_2 bond dissociation (580 K) suggests that below this temperature the Cu(II) complex is not completely destroyed. So, in the anhydrous compound the Cu(II) complex has probably a square planar configuration.

III. STRUCTURE DETERMINATION

1. Crystal Data

The main crystallographic features of the title compound, the parameters used for the X-ray diffraction data collection, and the strategy used for the crystal structure determination and its final results are reported in Table 2.

The final atomic coordinates and the equivalent temper-

ature factors for nonhydrogen atoms and B_{iso} for H atoms are given in Table 3. The values of the thermal anisotropic displacement parameters for non-H atoms and the list of observed and calculated structure factors are available on request.

2. Structure Description

This atomic arrangement is a typical layered organization built by two types of layers. The first type of layers, approximately centered by planes $z = \frac{1}{4}$ and $\frac{3}{4}$, consists of the HP_2O_7 phosphoric groups and one of the two crystallographic independent water molecules (OW2) not involved in the copper coordination polyhedron. The second type of layer includes the copper atoms, the second water molecule, the ethylenediammonium groups, and the ethylenediamine molecules. These layers are centered by planes $z = 0$ and $\frac{1}{2}$ and alternate with the first layers.

TABLE 2

Main Crystallographic Features, Parameters Used for the X-Ray Diffraction Data Collection, Strategy Used for the Crystal Determination and Its Final Results

Crystal data	
Formula: Cu ₂ C ₆ H ₂₆ N ₆ (HP ₂ O ₇) ₂ · 3H ₂ O	
$F_w = 713.343$	
Crystal system monoclinic Space group: $C2/c$	
$a = 18.808(8) \text{ \AA}; b = 9.631(2) \text{ \AA} V = 2392(4) \text{ \AA}^3$	
$c = 14.019(8) \text{ \AA}; \beta = 109.63(5)^\circ Z = 4$	
$\rho_{\text{cal.}} = 1.981 \text{ g} \cdot \text{cm}^{-3} F(000) = 1464$	
$\rho_{\text{obs.}} = 2.03 \text{ g} \cdot \text{cm}^{-3}$	
Linear absorption factor: $\mu(\text{AgK}\alpha) = 1.148 \text{ mm}^{-1}$	
Morphology: Intense blue multifaceted prism	
Crystal size: $0.32 \times 0.32 \times 0.32 \text{ mm}$	
Intensity measurements	
Temperature: 294 K	Wavelength: AgK α (0.5608 \AA)
Diffractometer: Philips PW1100	Scan mode: ω
Monochromator: graphite plate	Scan width: 1.20°
Scan speed: $0.02^\circ \cdot \text{sec}^{-1}$	Theta range: $3\text{--}30^\circ$
Total background measuring time: 10 sec	
Number of scans by reflection: 1	
Measurement area: $\pm h, k, l$	$h_{\text{max.}} = 32; k_{\text{max.}} = 17; l_{\text{max.}} = 24$
Total number of scanned reflections: 7590	
Total number of nonzero reflections: 4593	
Number of collected unique reflections: 4460 ($R_{\text{int}} = 0.015$)	
Reference reflections: 12 0 2, -12 0 -2: every 4 hr: no variation	
Structure determination	
Lorentz polarization corrections: no absorption correction	
Program used: SDP [9]	Computer used: Micro-Vax II
Determination: Direct Methods with MULTAN (10)	
Unique reflections included: 3917 with $I > 3\sigma(I)$	
Weighting scheme: unitary	Refined parameters: 227
Secondary extinction coefficient: Not applied	
Unweighted agreement factor R : 0.036 (R_w : 0.038)	
Weighted agreement factor R : 0.038	
Esd: 1.123	Large shift/error = 0.33
Max. residual density: $0.31 e \cdot \text{\AA}^{-3}$	
Drawing made with STRUPLO (11)	

Figure 2, depicting this arrangement in projection along the **a** direction, is not suitable for the understanding of this structure, but shows clearly the layered organization of its various components.

A layer of the first type, that centered by plane $z = 0.25$, is depicted in Fig. 3, its projection along the **c** direc-

TABLE 3

Final Atomic Coordinates and $B_{\text{eq.}}$ (\AA^2) for Nonhydrogen Atoms, $B_{\text{iso.}}$ (\AA^2) for Hydrogen Atoms

Atoms	x	y	z	$B_{\text{eq.}}$
Cu	0.00903(2)	-0.26451(3)	-0.06438(2)	1.401(4)
P(1)	0.12149(3)	-0.43070(6)	0.72625(4)	1.381(9)
P(2)	-0.13501(3)	-0.13063(6)	-0.22380(5)	1.369(9)
O(L12)	-0.1323(1)	-0.2796(2)	0.7236(1)	1.65(3)
O(E11)	0.0526(1)	-0.4252(2)	0.6320(2)	1.98(3)
O(E12)	0.1912(1)	-0.4542(2)	0.6922(1)	2.05(3)
O(E13)	0.1186(1)	-0.4700(2)	0.3056(1)	2.07(3)
O(E21)	0.4298(1)	-0.3701(2)	0.3759(2)	2.18(3)
O(E22)	0.2105(1)	0.8794(2)	0.7082(1)	2.07(3)
O(E23)	0.3733(1)	-0.4723(2)	0.1999(1)	2.04(3)
O(W1)	0.0185(1)	-0.2987(3)	0.4151(2)	3.05(4)
O(W2)	0	0.1259(3)	$\frac{1}{2}$	2.80(6)
N(1)	0.8057(1)	0.7786(2)	0.1372(2)	1.84(3)
N(2)	-0.4148(1)	-0.3881(2)	0.4894(2)	2.03(4)
N(3)	-0.0987(1)	-0.3903(2)	0.5200(2)	1.71(3)
C(1)	0.7241(2)	0.6929(3)	0.9728(2)	2.44(5)
C(2)	0.8475(2)	0.1768(3)	0.9356(2)	2.32(5)
C(3)	0.8311(1)	0.6908(3)	0.4811(2)	2.01(4)
Atoms	x	y	z	$B_{\text{iso.}}$
H	0.279(2)	0.010(5)	0.275(3)	5(1)
H(1N1)	0.765(2)	0.243(4)	0.660(3)	3.9(9)
H(2N1)	0.839(2)	0.291(5)	0.656(3)	5(1)
H(3N1)	0.169(2)	0.856(5)	0.334(3)	4(1)
H(1N2)	0.430(2)	0.546(4)	0.978(3)	4.0(9)
H(2N2)	0.902(2)	0.077(4)	0.064(3)	3.7(9)
H(1N3)	0.908(2)	0.446(4)	0.981(3)	4(1)
H(2N3)	0.606(2)	0.053(5)	0.928(3)	5(1)
H(1C1)	0.242(2)	0.607(5)	0.512(3)	5(1)
H(2C1)	0.812(2)	0.833(5)	0.006(3)	5(1)
H(1C2)	0.806(2)	0.110(4)	0.917(3)	3.3(8)
H(2C2)	0.361(2)	0.301(4)	0.376(3)	4(1)
H(1C3)	0.295(2)	0.862(4)	0.935(3)	3.0(8)
H(2C3)	0.687(2)	0.780(4)	0.464(3)	3.0(8)
H(1W1)	0.995(2)	0.629(5)	0.114(3)	6(1)
H(2W1)	0.497(2)	0.256(5)	0.138(3)	5(1)
H(W2)	0.539(2)	0.577(5)	0.766(3)	6(1)

Note. Estimated standard deviations are given in parentheses. $B_{\text{eq.}} = \frac{1}{3} \sum_i \sum_j a_i \cdot b_j \cdot b_{ij}$.

tion. Each HP₂O₇ group is connected to its two adjacent neighbors by strong hydrogen bonds (O–O = 2.491 \AA) so as to build a zigzag infinite (HP₂O₇)_n chain parallel to the **b** direction. In addition, the two chains spreading in this layer are themselves interconnected by the H-bonds created by the water molecule. The HP₂O₇ group involved in such a layer has no internal symmetry and in fact no specific features when compared with what is commonly measured for this type of anionic entity. Its main geometrical features are reported in Table 4.

Figure 4 shows, in projection along the **c** direction, the organization of a layer of the second type. Rows of copper atoms, ethylenediamine and water molecules, and ethylenediammonium groups parallel to the **a** direction alter-

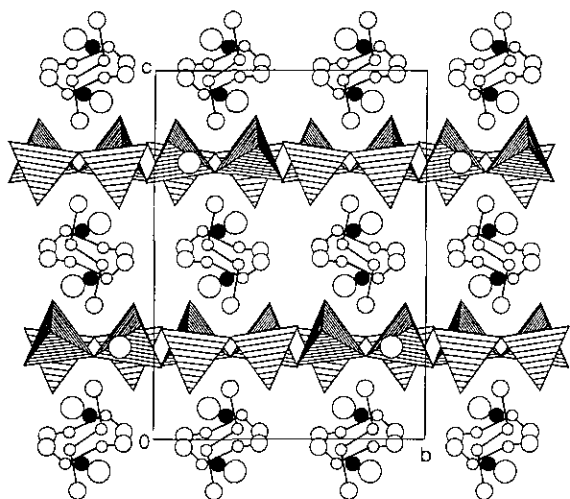


FIG. 2. Projection along the *a* direction of the atomic arrangement. The diphosphate groups are given with a polyhedral representation. Black circles represent copper atoms and by order of decreasing sizes empty circles represent water molecules, nitrogen, and carbon atoms. Hydrogen atoms have been omitted.

nate in planes $y = (2n + 1)/4$. One of the main characteristics of the title compound is the coexistence of both ethylenediammonium groups, $[\text{NH}_3-(\text{CH}_2)_2-\text{NH}_3]^{2+}$, and ethylenediamine molecules, $\text{NH}_2-(\text{CH}_2)_2-\text{NH}_2$. These two entities, whose main geometrical features are given in Table 4, do not differ significantly from what is usually reported for these kinds of groups.

According to recent studies (12), there are many stable five-coordinated complexes, particularly for d^7 , d^8 , and d^9 configurations. In a number of complexes the fivefold coordination is more or less forced upon the metal by the

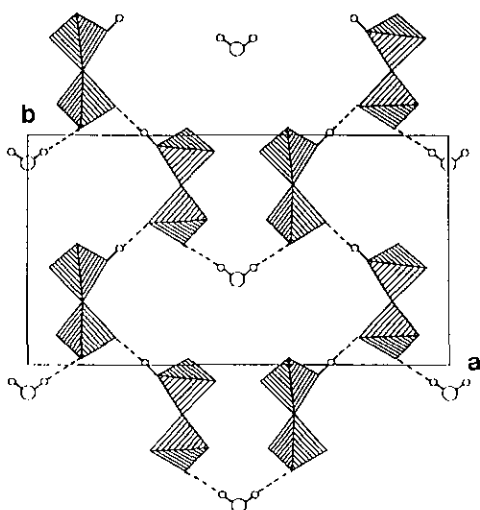


FIG. 3. Projection along the *c* direction of the layer of the first type located around the plane $z = \frac{1}{4}$. The P_2O_7 groups are given with a polyhedral representation. The larger empty circles represent the water molecules, the smaller the hydrogen atoms. Hydrogen bonds are denoted by full and dotted lines.

TABLE 4
Main Interatomic Distances (Å) and Bond Angles (°) for the Phosphoric Group, the Copper Polyhedron, the Ethylenediammonium Group, and the Ethylenediamine Molecule

Phosphoric group				
P(1)O ₄ tetrahedron				
P(1)	O(L12)	O(E11)	O(E12)	O(E13)
O(L12)	1.599(2)	107.33(9)	105.8(1)	106.8(1)
O(E11)	2.504(2)	1.509(2)	107.5(1)	116.3(1)
O(E12)	2.515(3)	2.471(2)	1.555(2)	112.6(1)
O(E13)	2.474(2)	2.540(2)	2.526(3)	1.481(2)
P(2)O ₄ tetrahedron				
P(2)	O(L12)	O(E21)	O(E22)	O(E23)
O(L12)	1.621(2)	106.6(1)	107.3(1)	103.5(1)
O(E21)	2.515(2)	1.515(2)	111.7(1)	114.1(1)
O(E22)	2.523(3)	2.504(2)	1.511(2)	112.8(1)
O(E23)	2.455(2)	2.491(2)	2.512(3)	1.504(2)
Copper polyhedron				
O(E11)-Cu-O(E21)	94.29	O(E11)-Cu-O(W1)	92.78(9)	
O(E11)-Cu-N(2)	168.8(1)	O(E11)-Cu-N(3)	88.40(8)	
O(E21)-Cu-O(W1)	96.41(9)	O(E21)-Cu-N(2)	91.16(8)	
O(E21)-Cu-O(N3)	170.0(1)	O(W1)-Cu-N(2)	96.37(9)	
O(W1)-Cu-N(3)	93.07(9)	N(2)-Cu-N(3)	84.63(9)	
Cu-O(E11)	1.974(2)	Cu-O(E21)	1.940(2)	
Cu-N(2)	2.013(2)	Cu-N(3)	1.999(2)	
Cu-O(W1)	2.342(2)			
Ethylenediammonium group				
C(1)-C(1)	1.497(4)	N(1)-C(1)-C(1)	110.4(2)	
C(1)-N(1)	1.478(3)			
Ethylenediamine molecule				
N(2)-C(2)	1.485(3)	N(2)-C(2)-C(3)	107.7(2)	
C(2)-C(3)	1.503(4)	C(2)-C(3)-N(3)	108.7(2)	
C(3)-N(3)	1.471(3)			

Note. Estimated standard deviations are given in parentheses.

geometric requirements of bonding to a chelate ligand in which two or more electron-pair donor atoms are located in such a way that they can donate to the same acceptor metal atoms. In this context, the copper atom of this structure has a fivefold coordination, a square pyramid, built up by a water molecule, two oxygen atoms belonging to the same HP_2O_7 anion, and two NH_2 groups of the ethylenediamine molecule. This organization we describe below reveals a stable chelate five-coordinated complex of the formula $[\text{Cu}(\text{C}_4\text{H}_8\text{N}_2)(\text{HP}_2\text{O}_7)(\text{H}_2\text{O})]^-$. Two bidentate ligands, ethylenediamine and acidic phosphoric anion, build the square basis of this pyramid while the independent donor atom, OW1, is located at its top, so two chelating five- and six-member rings contribute to the copper complex stability. The sum of the $\text{O}(\text{N})-\text{Cu}-\text{O}(\text{N})$ angles, 358.5° , close to 360° , indicates that the Cu atom is located in the square basis of the pyramid. Figure 5 depicts the arrangement we described above.

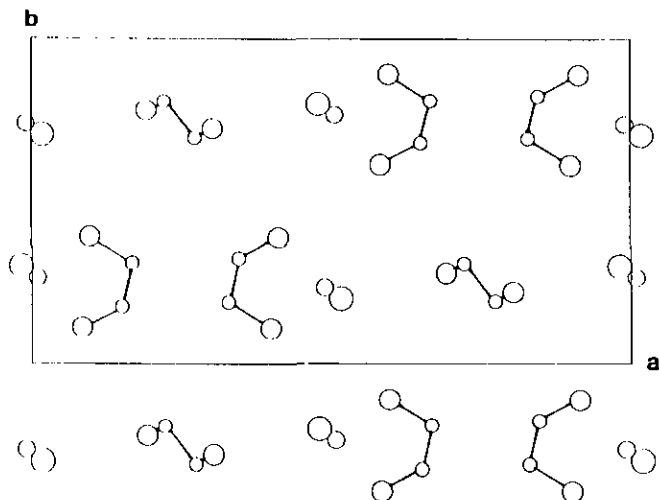


FIG. 4. Projection along the c direction ($0.28 < z < 0.72$) of the layer of the second type located around the plane $z = \frac{1}{2}$. By order of decreasing sizes the empty circles represent water molecules, nitrogen, copper, and carbon atoms. Hydrogen atoms have been omitted.

A three-dimensional network of hydrogen bonds reported in Table 5 interconnects the various components of this arrangement.

IV. IR SPECTROSCOPIC INVESTIGATION

IR absorption was carried out on a Shimadzu CHART 200-91527 spectrometer. Samples were dispersed in KBr and scanning was performed in the 4000–200 cm^{-1} spectral domain with a resolution of about 3 cm^{-1} .

The number of normal modes of vibrations in an isolated P₂O₇ group with an ideal D_{3h} symmetry is given by the representation $\Gamma_{\text{int}} = 3A'_1 + 4E' + A''_1 + 3A''_2 + 3E''$, while

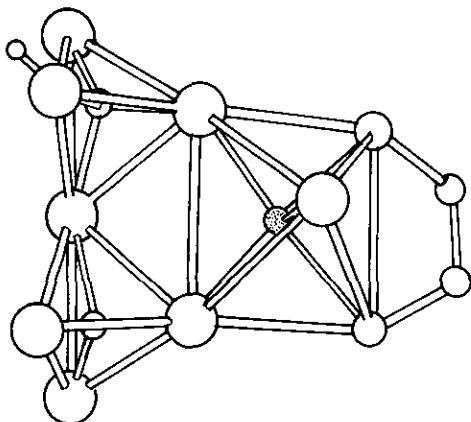


FIG. 5. Projection along the $[1\ 0\ 2]$ direction of the organization of the various ligands around the copper atom. Bonds in the square pyramid and the phosphoric group are drawn. By order of decreasing sizes the empty circles represent oxygen, nitrogen, carbon, copper, phosphorus, and hydrogen atoms.

TABLE 5
Hydrogen Bonds in Cu₂(C₂N₂H₁₀)(HP₂O₇)₂(C₂N₂H₈)₂ · 3H₂O

O(N)–H...O	O(N)–H	H...O	O(N)–O	O(N)–H...O
OE12–H...OE22	0.80(4)	1.69(4)	2.491(2)	175(5)
OW1–H1W1...OE11	0.80(5)	2.22(5)	2.950(3)	152(5)
OW1–H2W1...OW2	0.88(4)	1.92(4)	2.776(3)	164(4)
OW2–HW2...OE23	0.83(4)	1.86(4)	2.690(2)	178(5)
N1–H1N1...OE22	0.94(4)	1.92(4)	2.776(3)	149(4)
N1–H2N1...OE13	0.90(4)	1.90(4)	2.763(3)	162(4)
N1–H3N1...OE23	0.90(4)	1.83(4)	2.720(3)	169(3)
N2–H1N2...OE21	0.88(4)	2.22(4)	3.070(3)	163(3)
N2–H2N2...OE23	0.92(4)	2.21(4)	3.115(3)	171(4)
N3–H1N3...OE11	0.80(4)	2.33(5)	3.113(3)	167(4)
H1W1–OW1–H2W1	98(4)(8)		HW2–OW2–HW2	111(4)

that of the isolated organic groups with C_{2h} symmetry is $\Gamma_{\text{int}} = 11A_g + 7B_g + 8A_u + 10B_u$. According to several spectroscopic studies on inorganic diphosphates, (13–21) and metallic complexes with ethylenediamine (22–24) or ethylenediammonium (2, 25), the IR spectrum of Cu₂[NH₃–(CH₂)₂–NH₃][NH₂–(CH₂)₂–NH₂]₂(HP₂O₇)₂ · 3H₂O (Fig. 6) can be decomposed into three regions:

TABLE 6
IR Frequencies of Polycrystalline of
Cu₂(C₂N₂H₁₀)(HP₂O₇)₂(C₂N₂H₈)₂ · 3H₂O

$\bar{\nu}$ (cm ⁻¹)	Attributions	$\bar{\nu}$ (cm ⁻¹)	Attributions	
3500 m	ν OH ₂ + ν NH ₃ ⁺ + ν NH ₂ + ν CH ₂	1480 vw	$\delta(\text{CH}_2) + \rho(\text{CH}_2) +$ $\omega(\text{CH}_2)$	
3290 vs		1456 w		
3250 s		1396 vw		
3160 vs		1370 w		
3000 m		1330 m		
2950 s		1318 m		
2900 m		1280 w		
2890 w		1190 vs		$\nu_{\text{as}}(\text{PO}_3)$
2850 m		1150 sh		
2770 m		1124 vs		
2680 m	1108 vs			
2590 w	1056 vs			
2500 w	1030 sh			
2400 vw	Bands of combination and harmonics	1010 s	$\nu_s(\text{PO}_3)$	
2360 vw		960 s	$\nu_{\text{as}}(\text{POP})$	
2300 vw		904 s	$\rho(\text{NH}_3^+, \text{NH}_2)$	
2160 vw		Bands of combination	796 w	
2070 vw			816 sh	
{ 1660 w 1612 s 1556 m }		δ OH ₂ + δ NH ₃ ⁺ + δ NH ₂	720 m	$\delta(\text{PO}_3)$
			608 vw	
			558 s	
			530 s	
			488 m	
		456 m		
		410 w		

Note. vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

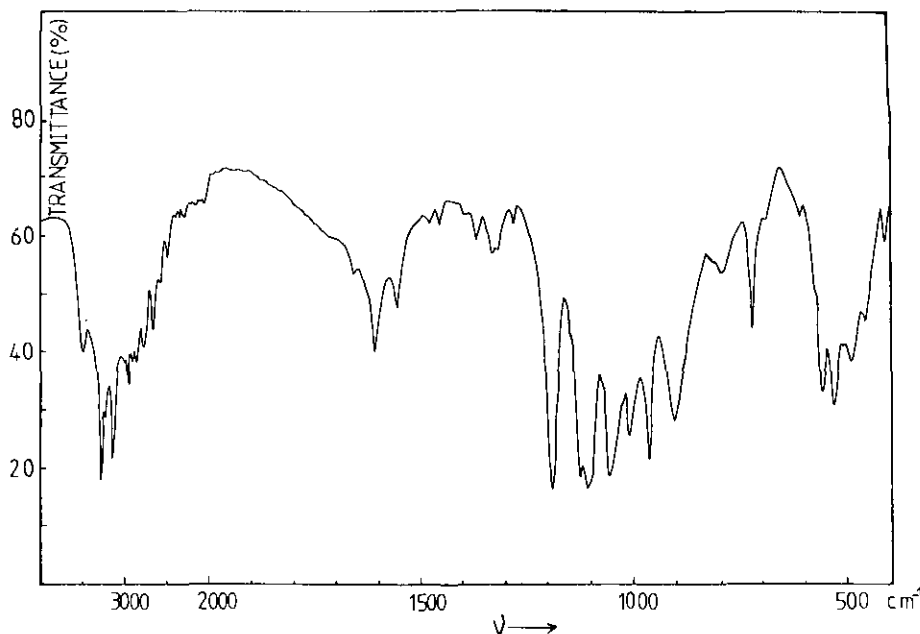


FIG. 6. IR spectrum of polycrystalline of $\text{Cu}_2(\text{C}_2\text{N}_2\text{H}_{10})(\text{HP}_2\text{O}_7)_2(\text{C}_2\text{N}_2\text{H}_8)_2 \cdot 3\text{H}_2\text{O}$.

40–300 cm^{-1} for the external modes of the anion and the cation, 300–1190 cm^{-1} for the internal modes of the anion, and 400–3400 cm^{-1} for the internal modes of the cation. According to the literature and to the group-theoretical analysis, we present in Table 6 an attempt to assign the different bands observed in these regions. In the crystal of the title compound, the 24 vibrations of the $\text{HP}_2\text{O}_7^{3-}$ anion with a bent configuration are distributed in 7 stretching modes and 13 bending modes for the PO_3 terminal groups and in 2 stretching modes and 2 bending modes for the POP bridge group. The stretching vibrations of the PO_3 terminal groups are observed between 975 and 1200 cm^{-1} (13, 14, 26), while those corresponding to POP modes occur between 740 and 950 cm^{-1} for the isolated diphosphate group with a bent geometry (27–29). Nevertheless, it must be pointed out that the assignment of the stretching vibrations, characteristic of CH_2 , NH_2 , and NH_3 groups, is not very easy because of the lack of deuterated compound and the Fermi resonance with the overtone of the corresponding asymmetric bending vibrations (25). By comparison with frequencies of other compounds including these groups (25, 29) we attribute, in Table 6, the remaining observed bands in the spectrum to the CH_2 , NH_2 , NH_3 , and H_2O symmetric, asymmetric stretching, and deformation modes.

V. CONCLUSION

Crystals of $\text{Cu}_2[\text{NH}_3-(\text{CH}_2)_2-\text{NH}_3][\text{NH}_2-(\text{CH}_2)_2-\text{NH}_2]_2(\text{HP}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ have been prepared by slow evaporation, at room temperature, of aqueous solutions of $\text{H}_4\text{P}_2\text{O}_7$, copper hydroxycarbonate, and ethylenediamine

in the proper ratios. The structure exhibits two types of layers. The HP_2O_7 groups are interconnected by strong hydrogen bonds to form an infinite $(\text{HP}_2\text{O}_7)_n$ chains. Hydrogen bonds from one of the two independent water molecules link two infinite chains so as to build the first type of layers. Copper atoms, ethylenediamine, and the second independent water molecule and ethylenediammonium groups constitute the second type of layers observed in the structure. Two bidentate ligands, ethylenediamine and $\text{HP}_2\text{O}_7^{3-}$ anion, and a water molecule, create with the copper atom a stable chelate five-coordinated complex, $[\text{Cu}(\text{C}_4\text{H}_8\text{N}_2)(\text{HP}_2\text{O}_7)(\text{H}_2\text{O})]^-$. The removal, by dehydration of the water molecules from the structure, leads to a blue anhydrous compound where Cu(II) complex has probably a square planar configuration. The infrared spectrum of the title compound shows well-resolved strong bands in the P_2O_7 and O(N)–H stretching regions, confirming the presence of diphosphate groups and strong hydrogen bonds.

REFERENCES

1. R. Masse and J. Zyss, *Molecular Engineering* **1**, 141 (1991).
2. S. Kammoun, A. Jouini, and A. Daoud, *J. Solid State Chem.* **99**, 18 (1992).
3. S. Kammoun, A. Jouini, M. Dabbabi, and A. Daoud, *Acta Crystallogr., Sect. C* **46**, 420 (1990).
4. M. T. Averbuch-Pouchot and A. Durif, *C.R. Acad. Sc., Paris*, **316**(2), 187 (1993).
5. A. Gharbi, DEA, Chimie Minérale, Université du Centre, Monastir, Tunisia, 1993.
6. G. Charlot, "Chimie Analytique Quantique," Vol. II. 1974.
7. T. Ozawa, *J. Therm. Anal.* **2**, 301 (1970).
8. H. E. Kissinger, *Anal. Chem.* **29**, 1702 (1957).

9. Structure Determination Package RSX11M, Enraf-Nonius, 1979.
10. P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, "Multan77, a System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data." Univ. of York, England, and Louvain, Belgium, 1977.
11. R. X. Fischer, *J. Appl. Crystallogr.* **18**, 258 (1985).
12. W. W. Porterfield, "Inorganic Chemistry." Addison-Wesley, Reading, MA, 1984.
13. A. N. Lazarev, "Vibrational Spectra and Structures of Silicates." Consultants Bureau, New York, 1972.
14. M. Gabelica-Robert and P. Tarte, *J. Mol. Struct.* **79**, 251 (1982).
15. M. Gabelica-Robert, *J. Mol. Struct.* **79**, 255 (1982).
16. M. Gabelica, *Spectrochim. Acta, Part A* **32**, 327 (1976).
17. D. E. C. Corbridge and J. Lowe, *J. Chem. Soc.*, 493 (1954).
18. W. G. Palmer, *J. Chem. Soc.*, 1552 (1961).
19. A. Hezel and S. D. Ross, *Spectrochim. Acta, Part A* **23**, 1583 (1967).
20. A. Hezel and S. D. Ross, *Spectrochim. Acta, Part A* **24**, 131 (1968).
21. E. Steger and G. Leukroth, *Z. Anorg. Allg. Chem.* **303**, 169 (1960).
22. M. Aliza, A. Bennett, A. Gary, and D. Thornton, *Spectrochim. Acta, Part A* **45**(2), 219 (1989).
23. M. Jouan, N. Quy Dao, and H. Brunet, *Spectrochim. Acta, Part A* **39**(11), 1021 (1983).
24. G. Diaz Fleming and R. E. Shepherd, *Spectrochim. Acta, Part A* **43**(9), 1141 (1987).
25. R. D. McLachlana, *Spectrochim. Acta, Part A* **30**, 985 (1974).
26. B. C. Cornilson, *J. Mol. Struct.* **117**, 1 (1984).
27. R. W. Mooney, S. Z. Toma, and J. Brunvoll, *Spectrochim. Acta, Part A* **23**, 1541 (1967).
28. R. W. Mooney and R. L. Goldsmith, *J. Inorg. Nucl. Chem.* **31**, 933 (1969).
29. Z. Iqbal, H. Arend, and P. Wachter, *J. Phys. C: Solid State Phys.* **14**, 1497 (1981).