

## A urea complex of copper(II) hypophosphite at 293, 100 and 15 K

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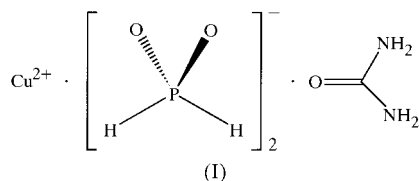
Received 4 December 2000

Accepted 15 March 2001

The crystal structure of poly[copper(II)-di- $\mu$ -hypophosphito- $\mu$ -urea],  $[\text{Cu}(\text{H}_2\text{PO}_2)_2(\text{CH}_4\text{N}_2\text{O})]_n$ , has been determined at 293, 100 and 15 K. The geometry of the hypophosphite anion is very close to ideal, with point symmetry  $mm2$ . Each Cu atom lies on an inversion centre and is coordinated to six O atoms from four hypophosphite anions and two urea molecules, forming a tetragonal bipyramid. The unique urea molecule lies on a twofold axis. Each hypophosphite anion in the structure is coordinated to two Cu atoms. The hypophosphite anions, urea molecules and  $\text{Cu}^{\text{II}}$  cations form polymeric ribbons. The  $\text{Cu}^{\text{II}}$  cations in the ribbon are linked together by two hypophosphite anions and a urea molecule, which is coordinated to Cu *via* an O atom. The ribbons are linked to each other by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds and form polymeric layers.

### Comment

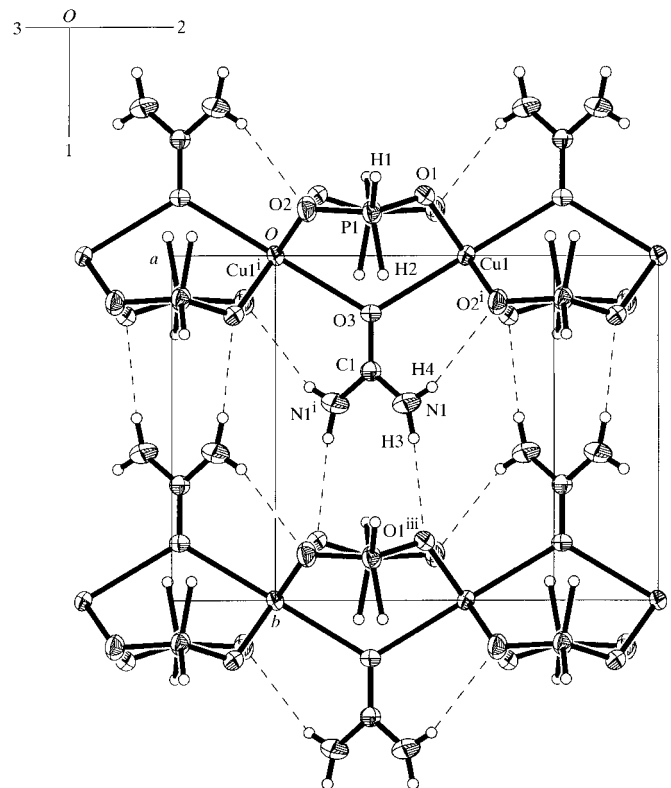
The present paper reports the results of a multiple-temperature single-crystal structural analysis of the urea complex of copper(II) hypophosphite, (I). No structural data for this compound have been reported previously, despite the great importance of the complex in many technological processes (Lomovsky & Boldyrev, 1994). The synthesis of the urea complex of copper(II) hypophosphite by adding different amounts of urea to copper(II) hypophosphite in solution was



described by Yagodin (1985, 1988). Our studies have shown that different starting ratios of the copper(II) hypophosphite and urea components (from 1:1 to 1:8) always give crystals with the same equal ratio (1:1) of copper(II) hypophosphite and urea.

The geometry of the hypophosphite anion in the crystal structure of (I) is very close to the ideal, with point symmetry  $mm2$ . Each Cu atom is coordinated to six O atoms from four hypophosphite anions and two urea molecules, forming a tetragonal bipyramid. Each hypophosphite anion in the structure is coordinated to two Cu atoms. Two different types of Cu–O bonds are observed. The hypophosphite anions, urea and  $\text{Cu}^{\text{II}}$  cations form polymeric ribbons in the [001] direction (Fig. 1). The  $\text{Cu}^{\text{II}}$  cations in the ribbon are linked together by two hypophosphite anions and a urea molecule, which is coordinated to Cu *via* an O atom. The ribbons are linked to each other *via*  $\text{N}-\text{H}\cdots\text{O}^{\text{iii}}$  hydrogen bonds [symmetry code: (iii)  $x, 1+y, z$ ] along the [010] direction and form polymeric layers in the (100) plane (Fig. 1). The urea molecule is rotated in a special way, to form an  $\text{N}-\text{H}\cdots\text{O}^{\text{i}}$  hydrogen bond [symmetry code: (i)  $x, -y, \frac{1}{2}+z$ ] with the nearest hypophosphite anion in the ribbon. The different layers are linked to each other by van der Waals interactions (Fig. 2).

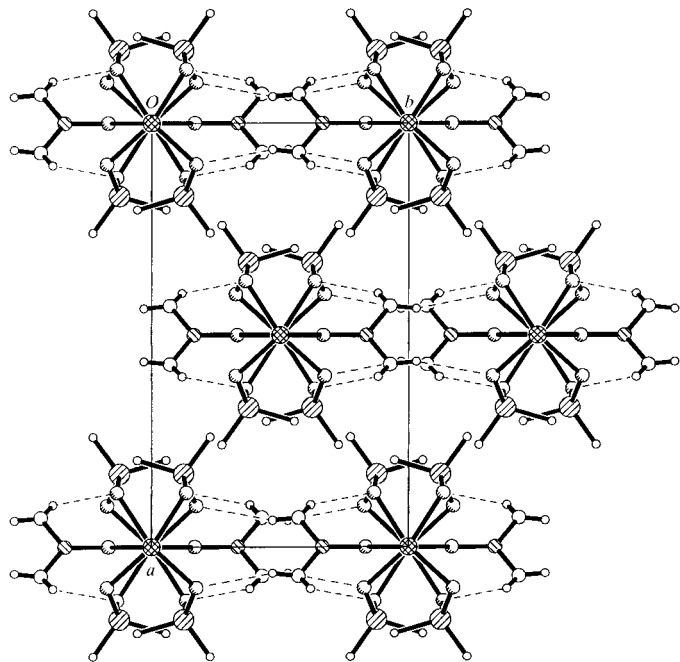
On cooling to 15 K, the structure of (I) contracts anisotropically. The contractions were calculated from the change in the cell parameters between 293 and 100 K, since the same diffractometer was used for data collection. On cooling from 100 to 15 K, the character of the contractions is the same. The direction of minimum contraction [0.297 (2)%; axis 1 of the



**Figure 1**

The layer formed by the  $\text{Cu}^{\text{II}}$  cations, hypophosphite anions and urea in (I) at 293 K projected on the (100) plane. Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. The crystallographic axes and the axes of the strain tensor on cooling (1 = minimum, 2 = medium, 3 = maximum contraction) are shown, and dotted lines indicate the  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds [symmetry codes: (i)  $x, -y, \frac{1}{2}+z$ ; (iii)  $x, 1+y, z$ ].

strain tensor in Fig. 1] coincides with the crystallographic *b* axis. The direction of this minimum contraction can be correlated with the N—H3···O1<sup>iii</sup> hydrogen bonds between different ribbons. The direction of medium contraction [0.321 (4)%; axis 2 of the strain tensor in Fig. 1] is close to the crystallographic *c* axis. The direction of the medium contraction can be correlated with the contraction of long Cu—O distances on cooling, and both these shorter contractions lie essentially within the layer. The direction of maximum contraction [1.620 (2)%; axis 3 of the strain tensor in Fig. 1] lies near the crystallographic *a* axis. This maximum contraction can be correlated with the decrease of the distance between layers in the crystallographic *a* direction.



**Figure 2**  
The packing diagram of the structure of (I) projected along [001]. Dotted lines indicate the N—H···O hydrogen bonds.

## Experimental

Compound (I) was synthesized by adding hypophosphorous acid, H<sub>3</sub>PO<sub>2</sub> (2.3771 g of 50% solution in 35 ml of water), to basic copper carbonate, CuCO<sub>3</sub>·Cu(OH)<sub>2</sub> (1 g). The reacting mixture was evacuated until carbon dioxide evolution had stopped (about 10 min). Next, a solution of urea (4.3852 g in 20 ml of water) was added to the solution of copper hypophosphite. The molar ratios of the three starting materials were 1:4:16 for basic copper carbonate, hypophosphorous acid and urea, respectively. Crystals of (I) were grown at 288 K from a solution in water under a nitrogen atmosphere.

### Compound (I) at 293 K

#### Crystal data

[Cu(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub>(CH<sub>4</sub>N<sub>2</sub>O)]  
*M<sub>r</sub>* = 253.57

Monoclinic, *C2/c*  
*a* = 12.5540 (3) Å  
*b* = 7.4686 (2) Å  
*c* = 8.2628 (3) Å  
*β* = 100.2722 (13)°  
*V* = 762.31 (4) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.209 Mg m<sup>-3</sup>  
Mo *Kα* radiation  
Cell parameters from 2732 reflections  
*θ* = 3.2–29.1°  
*μ* = 3.26 mm<sup>-1</sup>  
*T* = 293 (2) K  
Irregular, blue  
0.54 × 0.30 × 0.22 mm

#### Data collection

Siemens SMART CCD area-detector diffractometer  
*ω* scans  
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.221, *T<sub>max</sub>* = 0.488  
2894 measured reflections

1014 independent reflections  
920 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.030  
*θ<sub>max</sub>* = 29.1°  
*h* = -17 → 17  
*k* = -10 → 10  
*l* = -10 → 11

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.026  
*wR* (*F*<sup>2</sup>) = 0.076  
*S* = 1.12  
1014 reflections  
70 parameters  
All H-atom parameters refined

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0471*P*)<sup>2</sup>]  
where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> < 0.001  
Δρ<sub>max</sub> = 0.40 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.73 e Å<sup>-3</sup>  
Extinction correction: *SHELXL97* (Sheldrick, 1997)  
Extinction coefficient: 0.026 (2)

**Table 1**

Selected geometric parameters (Å, °) for (I) at 293 K.

Cu1—O1	1.9784 (14)	P1—O2	1.5119 (15)
Cu1—O2 <sup>i</sup>	1.9895 (14)	P1—H1	1.32 (3)
Cu1—O3	2.4153 (10)	P1—H2	1.42 (4)
Cu1—Cu1 <sup>ii</sup>	4.13140 (15)	O3—C1	1.256 (3)
P1—O1	1.5184 (15)	C1—N1	1.344 (3)
O1—Cu1—O2 <sup>i</sup>	90.34 (6)	P1—O2—Cu1 <sup>ii</sup>	125.38 (9)
O1—Cu1—O3	87.04 (5)	C1—O3—Cu1	121.21 (4)
O2 <sup>i</sup> —Cu1—O3	91.72 (5)	Cu1 <sup>ii</sup> —O3—Cu1	117.57 (8)
O1—P1—O2	117.84 (8)	O3—C1—N1	120.97 (15)
P1—O1—Cu1	123.82 (8)	N1—C1—N1 <sup>ii</sup>	118.1 (3)
N1—C1—O3—Cu1	47.74 (12)		

Symmetry codes: (i) *x*, -*y*, ½ + *z*; (ii) -*x*, *y*, ½ - *z*.

**Table 2**

Hydrogen-bonding geometry (Å, °) for (I) at 293 K.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H4···O2 <sup>i</sup>	0.75 (5)	2.36 (5)	3.037 (3)	152 (4)
N1—H3···O1 <sup>iii</sup>	0.77 (3)	2.27 (4)	3.021 (3)	162 (3)

Symmetry codes: (i) *x*, -*y*, ½ + *z*; (iii) *x*, 1 + *y*, *z*.

### Compound (I) at 100 K

#### Crystal data

[Cu(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub>(CH<sub>4</sub>N<sub>2</sub>O)]

*M<sub>r</sub>* = 253.57  
Monoclinic, *C2/c*  
*a* = 12.3589 (3) Å  
*b* = 7.4464 (2) Å  
*c* = 8.2199 (2) Å  
*β* = 99.8369 (14)°  
*V* = 745.35 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.260 Mg m<sup>-3</sup>  
Mo *Kα* radiation  
Cell parameters from 2798 reflections  
*θ* = 3.2–29.1°  
*μ* = 3.34 mm<sup>-1</sup>  
*T* = 100 (2) K  
Irregular, blue  
0.54 × 0.30 × 0.22 mm

#### Data collection

Siemens SMART CCD area-detector diffractometer  
*ω* scans  
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.297, *T<sub>max</sub>* = 0.480  
2849 measured reflections

996 independent reflections  
935 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.020  
*θ<sub>max</sub>* = 29.1°  
*h* = -16 → 16  
*k* = -10 → 10  
*l* = -10 → 11

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 0.9238P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.12$	$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$
996 reflections	$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$
70 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.0104 (9)

**Table 3**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I) at 100 K.

Cu1—O1	1.9788 (12)	P1—O2	1.5198 (13)
Cu1—O2 <sup>i</sup>	1.9901 (12)	P1—H1	1.32 (2)
Cu1—O3	2.3917 (8)	P1—H2	1.38 (3)
Cu1—Cu1 <sup>ii</sup>	4.1100 (1)	O3—C1	1.264 (3)
P1—O1	1.5236 (12)	C1—N1	1.3502 (19)
O1—Cu1—O2 <sup>i</sup>	90.45 (5)	P1—O2—Cu1 <sup>ii</sup>	124.56 (7)
O1—Cu1—O3	87.06 (4)	C1—O3—Cu1	120.77 (3)
O2 <sup>i</sup> —Cu1—O3	91.56 (4)	Cu1 <sup>ii</sup> —O3—Cu1	118.46 (7)
O1—P1—O2	117.66 (7)	O3—C1—N1	120.74 (11)
P1—O1—Cu1	122.76 (7)	N1—C1—N1 <sup>iii</sup>	118.5 (2)
N1—C1—O3—Cu1	48.15 (8)		

Symmetry codes: (i)  $x, -y, \frac{1}{2} + z$ ; (ii)  $-x, y, \frac{1}{2} - z$ .

**Table 4**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I) at 100 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H4 $\cdots$ O2 <sup>i</sup>	0.85 (3)	2.23 (3)	3.005 (2)	153 (2)
N1—H3 $\cdots$ O1 <sup>iii</sup>	0.78 (3)	2.23 (3)	2.998 (2)	169 (3)

Symmetry codes: (i)  $x, -y, \frac{1}{2} + z$ ; (iii)  $x, 1 + y, z$ .

## Compound (I) at 15 K

### Crystal data

$[\text{Cu}(\text{H}_2\text{PO}_4)_2(\text{CH}_4\text{N}_2\text{O})]$	$D_x = 2.280 \text{ Mg m}^{-3}$
$M_r = 253.57$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 24 reflections
$a = 12.297 (3) \text{ \AA}$	$\theta = 8-12^\circ$
$b = 7.435 (1) \text{ \AA}$	$\mu = 3.37 \text{ mm}^{-1}$
$c = 8.197 (2) \text{ \AA}$	$T = 15 (1) \text{ K}$
$\beta = 99.72 (1)^\circ$	Irregular, blue
$V = 738.7 (3) \text{ \AA}^3$	$0.27 \times 0.21 \times 0.15 \text{ mm}$
$Z = 4$	

### Data collection

$F_{\text{ddd}}$ (Copley <i>et al.</i> , 1997) diffractometer	$R_{\text{int}} = 0.025$
$\omega$ scans	$\theta_{\text{max}} = 29.1^\circ$
Absorption correction: empirical ( <i>XPREP</i> ; Siemens, 1995)	$h = -16 \rightarrow 16$
$T_{\text{min}} = 0.407, T_{\text{max}} = 0.604$	$k = -1 \rightarrow 10$
1355 measured reflections	$l = -2 \rightarrow 11$
993 independent reflections	3 standard reflections
980 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 1.2895P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.063$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.23$	$\Delta\rho_{\text{max}} = 0.99 \text{ e } \text{\AA}^{-3}$
993 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e } \text{\AA}^{-3}$
69 parameters	
All H-atom parameters refined	

**Table 5**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I) at 15 K.

Cu1—O1	1.9771 (12)	P1—O2	1.5186 (13)
Cu1—O2 <sup>i</sup>	1.9889 (12)	P1—H1	1.29 (2)
Cu1—O3	2.3824 (10)	P1—H2	1.37 (3)
Cu1—Cu1 <sup>ii</sup>	4.0985 (10)	O3—C1	1.265 (3)
P1—O1	1.5218 (12)	C1—N1	1.3486 (19)
O1—Cu1—O2 <sup>i</sup>	90.48 (5)	P1—O2—Cu1 <sup>ii</sup>	124.48 (7)
O1—Cu1—O3	87.08 (4)	C1—O3—Cu1	120.66 (4)
O2 <sup>i</sup> —Cu1—O3	91.59 (4)	Cu1 <sup>ii</sup> —O3—Cu1	118.67 (7)
O2 <sup>ii</sup> —Cu1—O3	88.41 (4)	O3—C1—N1	120.70 (11)
O1—P1—O2	117.57 (7)	N1—C1—N1 <sup>iii</sup>	118.6 (2)
P1—O1—Cu1	122.50 (7)		
N1—C1—O3—Cu1	48.23 (8)		

Symmetry codes: (i)  $x, -y, \frac{1}{2} + z$ ; (ii)  $-x, y, \frac{1}{2} - z$ .

**Table 6**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I) at 15 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H4 $\cdots$ O2 <sup>i</sup>	0.78 (3)	2.27 (3)	2.9963 (19)	155 (3)
N1—H3 $\cdots$ O1 <sup>iii</sup>	0.83 (3)	2.18 (3)	2.991 (2)	166 (2)

Symmetry codes: (i)  $x, -y, \frac{1}{2} + z$ ; (iii)  $x, 1 + y, z$ .

For compound (I) at 293 and 100 K, data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*. For compound (I) at 15 K, data collection: *MAD* (Allibon, 1996); cell refinement: *RAFIN* (Filhol *et al.*, 1987); data reduction: *COLLSN* (Lehmann & Wilson, 1987). For compound (I) at all three temperatures, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994).

The experimental study was carried out at the University of Durham. Financial support from the Royal Society, London (for DYN), and from the Russian Foundation for Basic Research (grant No. 99-03-32783) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1072). Services for accessing these data are described at the back of the journal.

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