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Diaquabis(2-hydroxyiminopropionato-κ^2N,O)copper(II)

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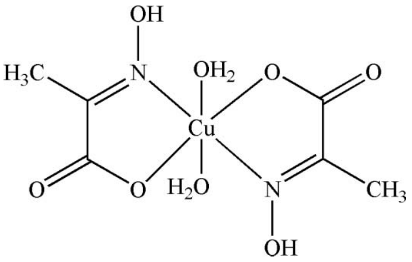
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.025; wR factor = 0.064; data-to-parameter ratio = 14.2.

The 100 K crystal structure of the title compound, $[Cu(C_3H_4NO_3)_2(H_2O)_2]$, is composed of discrete $[Cu(hipa)_2(H_2O)_2]$ units (hipa = 2-hydroxyiminopropionate). The Cu^{II} atom lies on an inversion centre and exhibits a slightly distorted octahedral coordination geometry formed by two chelating bidentate hipa ligands occupying equatorial sites and two water molecules in axial positions. The hipa ligands are bound to the copper centre in a *trans* fashion, generating a planar $\{Cu(hipa)_2\}$ core with the six-membered chelate rings having Cu—O and Cu—N distances of 1.9421 (13) and 2.0488 (15) Å, respectively, and N—Cu—O bite angles of 80.70 (6)°. The bonding parameters agree with those of the 298 K crystal structure of the title compound, which has been deposited at the Cambridge Structural Database (refcode IGUZAL) [Holt (2002). Private communication to the Cambridge Structural Database. Cambridge Crystallographic Data Centre, Cambridge, England] but remained unpublished. In the title compound, each water molecule acts as both an intermolecular hydrogen-bond donor (to the carboxylate O atoms) or acceptor (of hydrogen from the hydroxyl oxygen), thus multiply linking neighbouring mononuclear units and forming polymeric hydrogen-bonded two-dimensional layers. They are further extended by means of weak intermolecular C—H···O hydrogen bonds between methyl groups and the hydroxyl O atoms of hipa. The shortest Cu···Cu separations within these layers are equal to the unit-cell dimensions. The hipa ligands in the title compound are derived from a copper-promoted fragmentation of *N*-hydroxy-2,2′-iminodipropionic acid.

Related literature

For general background, see: Berry *et al.* (1999); Reis *et al.* (2005); Kirillov *et al.* (2006); Nesterov *et al.* (2006). For related structures, see: Malek *et al.* (2004); Dobosz *et al.* (1999). For examples of the fragmentation of *N*-hydroxy-2,2′-iminodipropionic acid, see: Kirillov *et al.* (2005); Harben *et al.* (1997).



Experimental

Crystal data

$[Cu(C_3H_4NO_3)_2(H_2O)_2]$
M_r = 303.72
Triclinic, $P\overline{1}$
a = 4.8204 (3) Å
b = 6.5447 (4) Å
c = 8.7092 (6) Å
α = 87.413 (4)°
β = 88.565 (5)°
γ = 74.939 (5)°
V = 265.02 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 2.10 mm^{-1}
T = 100 (2) K
0.37 × 0.14 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 2001)
T_{min} = 0.509, T_{max} = 0.867
2320 measured reflections
1207 independent reflections
1170 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.064
S = 1.10
1207 reflections
85 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.9421 (13)	Cu1—O4	2.4090 (14)
Cu1—N1	2.0488 (15)		
O3—Cu1—N1	80.69 (6)	N1—Cu1—O4	88.44 (5)
O3—Cu1—O4	90.72 (5)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O4^{i}	0.88 (3)	1.74 (3)	2.6207 (19)	173 (3)
O4—H4A···O3^{ii}	0.85	2.00	2.6319 (18)	130
O4—H4B···O2^{iii}	0.85	1.82	2.6638 (18)	170
C2—H2C···O1^{iv}	0.98	2.57	3.535 (3)	169

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y, -z$; (iii) $x, y-1, z$; (iv) $-x, -y, -z+1$.

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure:

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SHELXL97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2012).

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supplementary materials

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Diaquabis(2-hydroxyiminopropionato-κ^2*N*,*O*)copper(II)

M. V. Kirillova, M. Haukka, A. M. Kirillov, J. A. L. Silva, J. J. R. Fraústo da Silva and **A. J. L. Pombeiro**

Comment

The *N*-hydroxy-2,2'-iminodipropionic acid (H_3hidpa), HON(CH(CH_3)COOH$_2$, constitutes, in its basic form hidpa^{3-}, the ligand in *Amavadine* (Berry *et al.*, 1999), a natural bare vanadium(IV) complex [V(hidpa)$_2$]$^{2-}$ which is present in some *Amanita* fungi and has been applied as an efficient catalyst in various alkane functionalization reactions (Reis *et al.*, 2005). Hence, in pursuit of these and other studies, namely focusing on the self-assembly synthesis of copper(II) complexes with various *N*,*O*-ligands and their application in catalysis (Kirillov *et al.*, 2006; Nesterov *et al.*, 2006), we have attempted the preparation of the copper compound structurally related to *Amavadine*. However, the reaction of $Cu(NO_3)_2\times2.5H_2O$ with H_3hidpa in methanol and at room temperature resulted in the formation of the title compound, (I), due to the fragmentation of H_3hidpa to give 2-hydroxyiminopropionate, HON=C(CH_3)COO$^-$ (hipa). Such a type of fragmentation is unusual or even unknown, although other examples of H_3hidpa fragmentations promoted by Re or Mo centres have already been described (Harben *et al.*, 1997; Kirillov, Haukka *et al.*, 2005). Herein we report the synthesis of compound (I) and its characterization by IR spectroscopy, elemental and low-temperature (100 K) single-crystal X-ray diffraction analyses.

The crystal structure of (I) (Fig. 1) is composed of discrete monomeric units, with a slightly distorted centrosymmetric octahedral geometry formed by two bidentate hipa ligands occupying equatorial sites and two water molecules in apical positions. Most of the bonding parameters in (I) (Table 1) agree with those of the related copper compounds (Malek *et al.*, 2004; Dobosz *et al.*, 1999) bearing hipa or derived moieties.

In (I), each water oxygen atom (O4) acts as both an intermolecular hydrogen-bond donor (to the carboxylate oxygen atoms O2 and O3) or acceptor (of hydrogen from the hydroxo oxygen O1) (Table 2), thus multiply linking the neighbouring mononuclear units and forming polymeric H-bonded chains (if seen along the *a* or *b* axis, Fig. 2a) or two-dimensional layers (if seen along the *c* axis, Fig. 2 b). These chains and layers are further extended by means of the weak intermolecular C2—H2C···O1 interactions resulting in a three-dimensional hydrogen bonded network.

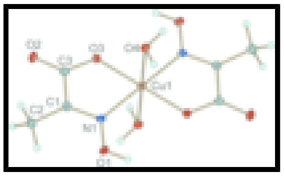
Experimental

To a methanolic solution (5 ml) of $Cu(NO_3)_2\times2.5H_2O$ (58 mg, 0.25 mmol) was added *N*-hydroxy-2,2'-iminodipropionic acid (44 mg, 0.25 mmol) with continuous stirring at room temperature. The reaction mixture was stirred overnight and then filtered. The filtrate was left in a vial to evaporate in air at ambient temperature. Green X-ray quality crystals were formed in several days and were collected and dried in air (yield 26%, based on copper nitrate). Analysis calculated for $C_6H_{12}CuN_2O_8$: C 23.73, H 3.98, N 9.22; found: C 23.77, H 4.10, N 8.84%. FT—IR, selected bands, cm^{-1}: 3306 [*s*,*br*, $\nu(H_2O)+\nu(OH)$], 2796 [*w*, ν(CH)], 1678 [*s*,*br*, $\nu_{as}(COO)+\nu(C=N)$], 1460 and 1361 [*s*, ν_s(COO)], 1386 [*w*, $\delta(CH_3)$], 1077 [*s*, ν(NO)].

Refinement

The hydrogen atoms H1O, H4A and H4B were located from the difference Fourier map. The H1O atom was refined isotropically and but the H4A and H4B atoms but were constrained to ride on their parent atom, with U_{iso} = 1.5 U_{eq}(parent atom). Other H atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C—H = 0.98 Å, and U_{iso} = 1.5 U_{eq}(parent atom). The highest peak is located 0.75 Å from atom C1 and the deepest hole is located 0.81 Å from atom Cu1.

Figures



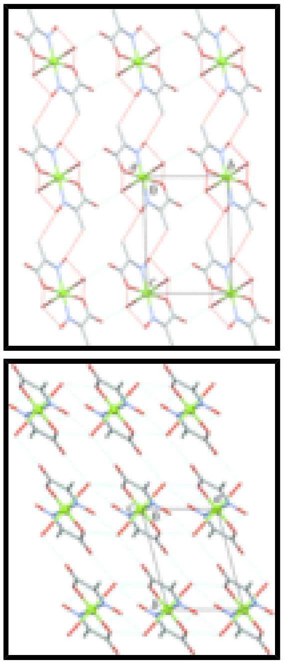


Fig. 1. The molecular structure of the title compound, showing the atom-labeling scheme. The suffixes A correspond to the symmetry position ($-x$, $-y$, $-z$). Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radii.

Fig. 2. Ball-and-stick partial representation of the crystal packing of compound (I), viewed down the *a* (*a*) and *c* (*b*) axis, with hydrogen-bonding network (dashed lines). H atoms are omitted for clarity. Cu, green; N, blue; O, red; C, grey.

Diaquabis(2-hydroxyiminopropionato-κ^2*N*,*O*)copper(II)

Crystal data

$[Cu(C_3H_4NO_3)_2(H_2O)_2]$	$Z = 1$
$M_r = 303.72$	$F_{000} = 155$
Triclinic, $P\bar{1}$	$D_x = 1.903$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71073 Å
$a = 4.8204$ (3) Å	Cell parameters from 2320 reflections
$b = 6.5447$ (4) Å	θ = 3.9–27.4°

$c = 8.7092$ (6) Å

$\alpha = 87.413$ (4)°

$\beta = 88.565$ (5)°

$\gamma = 74.939$ (5)°

$V = 265.02$ (3) Å^3

$\mu = 2.10$ mm^{-1}

$T = 100$ (2) K

Plate, pale green

0.37 × 0.14 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: horizontally mounted graphite crystal

Detector resolution: 9 pixels mm^{-1}

$T = 100(2)$ K

φ scans and ω scans with κ offset

Absorption correction: multi-scan (XPREP in SHELXTL; Sheldrick, 2001)

$T_{\text{min}} = 0.509$, $T_{\text{max}} = 0.867$

2320 measured reflections

1207 independent reflections

1170 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\text{max}} = 27.4$°

$\theta_{\text{min}} = 3.9$°

$h = -6\rightarrow6$

$k = -8\rightarrow8$

$l = -11\rightarrow11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.064$

$S = 1.10$

1207 reflections

85 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 0.2627P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.42$ e Å^{-3}

$\Delta\rho_{\text{min}} = -0.56$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.0000	0.0000	0.0000	0.01113 (12)
O1	−0.3635 (3)	−0.0415 (2)	0.29803 (15)	0.0142 (3)
H1O	−0.430 (6)	−0.118 (4)	0.235 (3)	0.030 (7)*
O2	0.1815 (3)	0.4394 (2)	0.24723 (16)	0.0161 (3)
O3	0.1601 (3)	0.2297 (2)	0.05499 (15)	0.0128 (3)
O4	0.3956 (3)	−0.2557 (2)	0.11946 (15)	0.0133 (3)
N1	−0.1846 (3)	0.0563 (2)	0.21363 (18)	0.0106 (3)
C1	−0.1067 (4)	0.1993 (3)	0.2845 (2)	0.0112 (3)
C2	−0.1950 (4)	0.2699 (3)	0.4424 (2)	0.0163 (4)
H2A	−0.3498	0.2080	0.4798	0.025*
H2B	−0.2630	0.4247	0.4406	0.025*
H2C	−0.0302	0.2235	0.5109	0.025*
C3	0.0944 (4)	0.3002 (3)	0.1904 (2)	0.0112 (3)
H4A	0.5075	−0.3129	0.0472	0.017*
H4B	0.3083	−0.3461	0.1542	0.017*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01162 (18)	0.01280 (17)	0.01097 (17)	−0.00651 (12)	0.00254 (11)	−0.00354 (11)
O1	0.0156 (7)	0.0183 (7)	0.0128 (6)	−0.0118 (5)	0.0037 (5)	−0.0022 (5)
O2	0.0209 (7)	0.0152 (7)	0.0158 (7)	−0.0105 (6)	0.0016 (5)	−0.0044 (5)
O3	0.0136 (7)	0.0149 (6)	0.0119 (6)	−0.0072 (5)	0.0027 (5)	−0.0034 (5)
O4	0.0127 (7)	0.0140 (6)	0.0148 (6)	−0.0065 (5)	0.0027 (5)	−0.0019 (5)
N1	0.0090 (7)	0.0126 (7)	0.0109 (7)	−0.0045 (6)	0.0013 (5)	−0.0006 (6)
C1	0.0102 (9)	0.0117 (8)	0.0117 (8)	−0.0028 (7)	0.0002 (6)	−0.0012 (6)
C2	0.0192 (10)	0.0186 (9)	0.0129 (9)	−0.0076 (8)	0.0034 (7)	−0.0054 (7)
C3	0.0100 (8)	0.0108 (8)	0.0127 (8)	−0.0023 (6)	−0.0003 (6)	−0.0007 (6)

Geometric parameters (Å, °)

Cu1—O3	1.9421 (13)	O3—C3	1.288 (2)
Cu1—O3^{i}	1.9421 (13)	O4—H4A	0.8527
Cu1—N1^{i}	2.0487 (15)	O4—H4B	0.8519
Cu1—N1	2.0488 (15)	N1—C1	1.282 (2)
Cu1—O4^{i}	2.4090 (14)	C1—C2	1.488 (2)
Cu1—O4	2.4090 (14)	C1—C3	1.514 (2)
O1—N1	1.3805 (19)	C2—H2A	0.9800
O1—H1O	0.88 (3)	C2—H2B	0.9800
O2—C3	1.225 (2)	C2—H2C	0.9800
O3—Cu1—O3^{i}	180	Cu1—O4—H4B	99.7
O3—Cu1—N1^{i}	99.31 (6)	H4A—O4—H4B	107.3
O3^{i}—Cu1—N1^{i}	80.69 (6)	C1—N1—O1	114.50 (15)

O3—Cu1—N1	80.69 (6)	C1—N1—Cu1	114.06 (12)
O3^{i}—Cu1—N1	99.31 (6)	O1—N1—Cu1	131.30 (11)
N1^{i}—Cu1—N1	180	N1—C1—C2	126.73 (17)
O3—Cu1—O4^{i}	89.28 (5)	N1—C1—C3	113.30 (15)
O3^{i}—Cu1—O4^{i}	90.72 (5)	C2—C1—C3	119.97 (16)
N1^{i}—Cu1—O4^{i}	88.44 (5)	C1—C2—H2A	109.5
N1—Cu1—O4^{i}	91.56 (5)	C1—C2—H2B	109.5
O3—Cu1—O4	90.72 (5)	H2A—C2—H2B	109.5
O3^{i}—Cu1—O4	89.28 (5)	C1—C2—H2C	109.5
N1^{i}—Cu1—O4	91.56 (5)	H2A—C2—H2C	109.5
N1—Cu1—O4	88.44 (5)	H2B—C2—H2C	109.5
O4^{i}—Cu1—O4	180	O2—C3—O3	125.38 (17)
N1—O1—H1O	107.5 (19)	O2—C3—C1	118.66 (16)
C3—O3—Cu1	115.88 (11)	O3—C3—C1	115.96 (15)
Cu1—O4—H4A	106.8		

Symmetry codes: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O4^{ii}	0.88 (3)	1.74 (3)	2.6207 (19)	173 (3)
O4—H4A···O3^{iii}	0.85	2.00	2.6319 (18)	130
O4—H4B···O2^{iv}	0.85	1.82	2.6638 (18)	170
C2—H2C···O1^{v}	0.98	2.57	3.535 (3)	169

Symmetry codes: (ii) *x*−1, *y*, *z*; (iii) −*x*+1, −*y*, −*z*; (iv) *x*, *y*−1, *z*; (v) −*x*, −*y*, −*z*+1.

Fig. 1

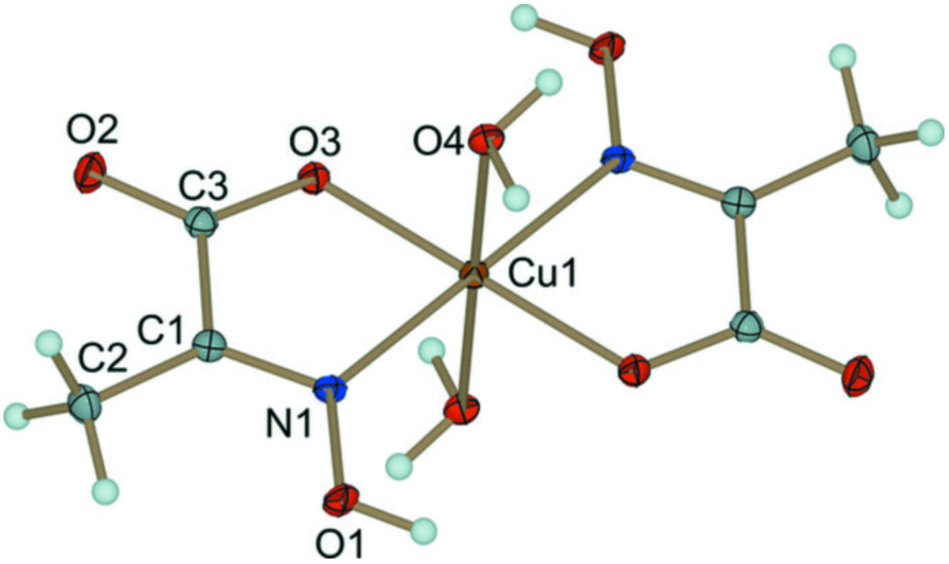


Fig. 2

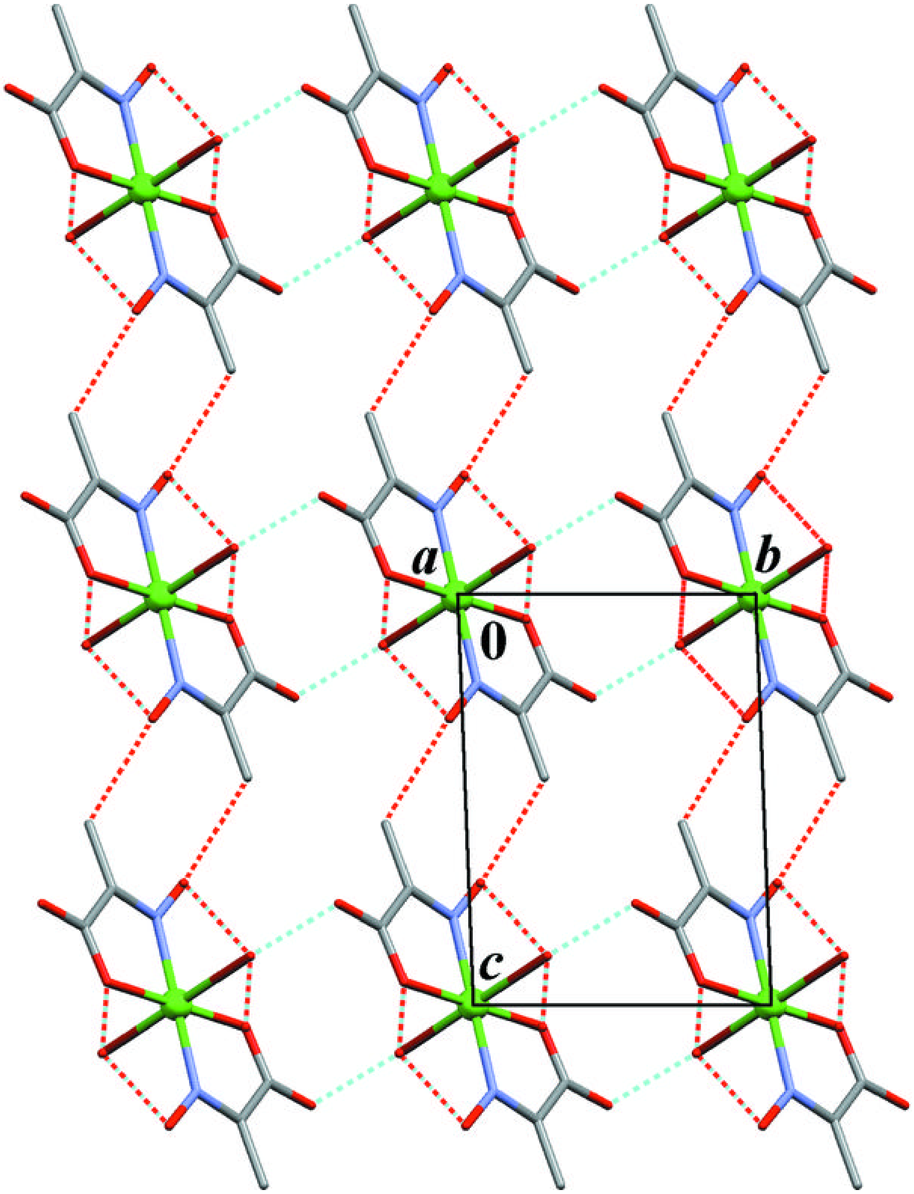


Fig. 3