

Article

The Synthesis and Characterization of the Novel Pseudo-Octahedral Complex bis[(2-hydroxybenzyl) - (2-methylpyridyl)-amine] zinc(II), $[Zn^{II}(bpa)_2] \cdot 2H_2O$ as a Model for Astacin

Ademir Neves*, Ivo Vencato, and Cláudio Nazari Verani

Departamento de Química, Universidade Federal de Santa Catarina,
88040-900 Florianópolis - SC, Brazil

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A reação entre o ligante (2-hidroxibenzil)(2-metilpiridil) amina (Hbpa) e $Zn(OAc)_2 \cdot 2H_2O$ (estequiometria 2:1), em solução metanólica, rendeu cristais incolores de $[Zn(bpa)_2]$. A estrutura cristalina do complexo foi determinada por difração de raios-X, no sistema cristalino triclinico, grupo espacial $P\bar{1}$ (No. 2) e dimensões de cela $a = 9,504(1)$, $b = 11,984(1)$ $c = 11,966(1)$ Å, $\alpha = 79,36(2)$, $\beta = 89,18(2)$, $\gamma = 78,95(2)^\circ$, $V = 1314,2(2)$ Å³, $Z = 2$, $D_{calc} = 1,334$ Mg m⁻³, $\lambda(MoK\alpha) = 0,71073$ Å, $\mu = 0,991$ mm⁻¹, $F(000) = 552$, $T = 296$ K, $R = 7,1\%$ ($R_w = 11,0\%$), com 4846 reflexões medidas, 3247 reflexões observadas com $I > 3\sigma(I)$ e 326 parâmetros refinados. A geometria de coordenação em torno do Zn(II) é pseudo-octaédrica com as unidades tripodais do ligante (bpa⁻) coordenadas facialmente. Segundo nosso conhecimento, $[Zn(bpa)_2] \cdot 2H_2O$ representa o primeiro exemplo estrutural de um complexo octaédrico de Zn^{2+} que contém fenolato na sua esfera de coordenação.

The reaction between (2-hydroxybenzyl)(2-pyridylmethyl) amine (Hbpa) and $Zn(OAc)_2 \cdot 2H_2O$ (2:1) in a methanolic medium gave colorless crystals of $[Zn(bpa)_2] \cdot 2H_2O$. The crystal structure of the complex was determined by X-ray diffraction in the triclinic crystal system, space group $P\bar{1}$ (No. 2), and cell dimensions $a = 9.504(1)$, $b = 11.984(1)$, $c = 11.966(1)$ Å, $\alpha = 79.36(2)$, $\beta = 89.18(2)$, $\gamma = 78.95(2)^\circ$, $V = 1314.2(2)$ Å³, $Z = 2$, $D_{calc} = 1.334$ Mg m⁻³, $\lambda(MoK\alpha) = 0.71073$ Å, $\mu = 0.991$ mm⁻¹, $F(000) = 552$, $T = 296$ K, and $R = 7.1\%$ ($R_w = 11.0\%$), with 4846 measured reflections and 3247 observed reflections with $I > 3\sigma(I)$ and 326 refined parameters. The coordination environment around the Zn(II) ion is pseudo-octahedral, with the tripodal units of bpa⁻ coordinated in a facial arrangement. To the best of our knowledge, $[Zn(bpa)_2] \cdot 2H_2O$ is the first structural example of an octahedral Zn^{2+} complex which contains phenolate in its coordination sphere.

Keywords: mononuclear zinc(II) complex, X-ray analysis, $[Zn(bpa)_2] \cdot 2H_2O$

Introduction

It is well known that zinc plays an important role in many biological processes¹. It is now evident that zinc is essential for the normal growth and development of all living matter, but, remarkably, this universal requirement has been unappreciated until quite recently^{1c}. Particularly of interest, are the extracellular zinc enzymes which are involved in hydrolytic processes. Astacin, a digestive zinc-endopeptidase from the crawfish *Astacus astacus* L.² represents the prototype for the "astacin family"³, which

includes mammalian metalloendopeptidases⁴ and developmentally regulated proteins of humans⁵, fruitflies⁶, frogs⁷ and sea urchins⁸. Very recently, the X-ray crystal structure of this metalloenzyme was solved and refined to a crystallographic R -value of 0.162 using reflections from 10 to 1.8 Å⁹. The structure of the active site reveals that the Zn^{2+} lies in a trigonal-bipyramidal coordination environment, with three histidines, a water molecule, and a remote tyrosine as ligands⁹. One histidine nitrogen and the tyrosine OH group, at distances of 2.3 and 2.6 Å from the zinc, respectively, are

apically connected, whereas the other three ligands are coplanar with, and 2.1 Å apart from, the central zinc. It is important to note that astacin represents the first example of a zinc enzyme which contains tyrosine ligated directly to the metal center in the active site⁹. In order to provide model compounds for this class of enzymes and subsequent reactivity and activity studies, we report here the synthesis and X-ray crystal structure of the $[\text{Zn}(\text{bpa})_2] \cdot 2\text{H}_2\text{O}$ complex which contains the tripodal Hbpa ligand (Fig. 1), with phenolate, amine, and pyridine coordinated to Zn^{2+} . This is part of our program for the preparation and characterization of metal complexes with bioinorganic relevance¹⁰.

Experimental

Materials

Salicylaldehyde, 2-(aminomethyl)pyridine, and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ were obtained from Aldrich Chemical Co. All other chemicals and solvents were reagent grade.

Syntheses

The ligand (2-hydroxybenzyl)(2-pyridylmethyl) amine (Hbpa) was obtained from a condensation reaction of 2-(aminomethyl)pyridine and salicylaldehyde followed by a reduction with NaBH_4 in methanol^{10c}. Yield: 65%. Mp = 62 °C (lit. value: 62 °C^{10c}).

$[\text{Zn}(\text{bpa})_2] \cdot 2\text{H}_2\text{O}$ (1)

$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.22 g, 1.0 mmol) was added to a solution of Hbpa (0.43 g, 2.0 mmol) in 15 mL of methanol. The clear solution was heated to 40 °C and stirred for 10 min at ambient atmosphere. After the solution was cooled to room temperature, ethylacetate (10 mL) was added, and in a few days suitable colorless crystals of 1 for X-ray crystallography were obtained. Anal. Calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_2\text{Zn} \cdot 2\text{H}_2\text{O}$: C, 59.15; H, 5.73; N, 10.61%. Found: C, 58.45; H, 6.58; N, 10.48%.

X-ray crystallography

A colorless prismatic single crystal with dimensions 0.20 x 0.30 x 0.70 mm was mounted on a glass fiber and used to collect data on a Nonius CAD-4 diffractometer¹¹ with graphite-monochromated $\text{Mo K}\alpha$ radiation and ω -2 θ scan. The unit cell and the orientation matrix for the data collection were obtained by a least-squares fit of 25 centered reflections ($17.56 < \theta < 19.57^\circ$). The intensities of three standard reflections were measured every 60 min and

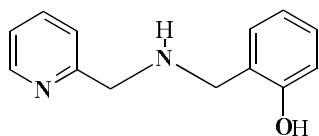


Figure 1. The ligand Hbpa = (2-hydroxybenzyl)(2-pyridylmethyl) amine.

varied less than 1.2%. The intensity data were corrected for Lorentz and polarization effects, but no decay correction was applied. A Ψ scan-based empirical absorption correction was applied (transmission factors 0.9695 to 0.9997). The number of measured reflections was 4846 in the range of -11/11, 0/14, -13/14, with 4608 unique reflections, and 3242 were above the significance level of $3\sigma(I)$. The maximum value of $(\sin \theta)/\lambda$ was 0.594 \AA^{-1} . Equivalent reflections were merged with $R_{\text{int}} = 2.2\%$. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The intensity statistics were consistent with a centrosymmetric space group. We solved and refined this structure in $P\bar{1}$, with two half molecules in the asymmetric unit because the two Zn atoms were found at inversion centers.

The structure was solved by means of direct methods using SIR92¹² and subsequent Fourier difference synthesis. The structure was refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$. A weighing scheme of $w = 1/[(\sigma(F_o)^2 + (0.020 \cdot F_o)^2 + 1.0)]$ was used. H atoms were placed in geometrically calculated positions with C-H = 0.95 Å, the aqua H atoms were found in difference Fourier maps and their parameters were not included in the refinement. Anisotropic displacement parameters were used for all non-hydrogen atoms; each H atom was given an isotropic displacement parameter equal to 1.3 times the equivalent isotropic displacement parameter of the atom to which it is attached. At the end of the refinement an isotropic extinction correction ($1 + gI_c$) was applied to F_c with a coefficient of $g = 2.48(1) \times 10^{-7}$. The number of refined parameters was 326, and the fit was 1.739. Residual densities of 1.32 and $-0.94 \text{ e}^-/\text{\AA}^3$ in the final difference map were found. Examination of the structure with PLATON¹³ showed no solvent-accessible voids in the crystal lattice. The final refinement gave $R = 7.1\%$, $R_w = 11.0\%$ and all parameter shifts were less than 0.12 of the corresponding standard deviation. Scattering factors were taken from the International Tables for X-ray Crystallography (1974). Calculations were performed on a DEC 3000 AXP computer using the MolEN package¹⁴.

Results and Discussion

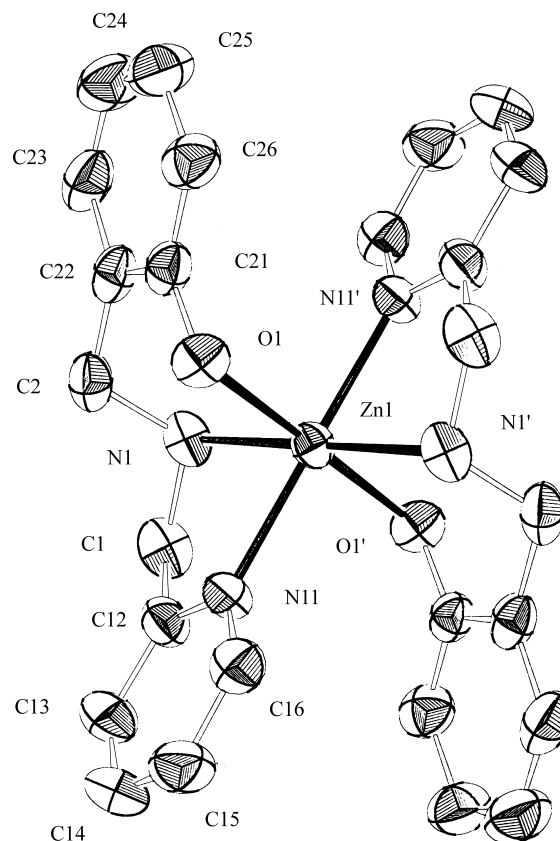
The Crystal and Molecular structure of $[\text{Zn}(\text{bpa})_2] \cdot 2\text{H}_2\text{O}$ (1)

The structure of complex 1 consists of discrete neutral $[\text{Zn}(\text{bpa})_2]$ units and water molecules of crystallization. The asymmetric unit consists of two slightly different half molecules, since the whole molecules are generated by distinct inversion centers. Table 1 reports the final atomic coordinates, while Fig. 2 shows the ORTEP¹⁵ of molecule 1 with an atom-numbering scheme. Bond distances and bond angles are given in Tables 2 and 3, respectively.

Table 1. Final positional parameters and equivalent isotropic temperature factors with e.s.d's in parentheses.

Atom	x	y	z	B(Å ²)
Zn1	0.000	1.000	0.0000	2.58(3)
O1	0.1631(7)	0.8526(6)	0.0679(6)	3.5(1)
N1	-0.1539(8)	0.8882(7)	0.0251(7)	3.0(2)
N11	0.0114(8)	0.9425(7)	-0.1612(7)	3.1(2)
C1	-0.215(1)	0.8934(9)	-0.089(1)	3.8(2)
C2	-0.090(1)	0.7689(8)	0.0795(9)	3.7(2)
C12	-0.104(1)	0.8983(8)	-0.1800(9)	3.5(2)
C13	-0.122(1)	0.862(1)	-0.2823(9)	4.7(3)
C14	-0.020(2)	0.875(1)	-0.3657(9)	5.3(3)
C15	0.093(1)	0.923(1)	-0.3457(9)	4.6(3)
C16	0.107(1)	0.9552(9)	-0.2428(9)	3.6(2)
C21	0.126(1)	0.8056(8)	0.1705(8)	3.1(2)
C22	-0.000(1)	0.7625(8)	0.1843(9)	3.3(2)
C23	-0.044(1)	0.7184(9)	0.294(1)	4.4(3)
C24	0.039(1)	0.714(1)	0.387(1)	5.2(3)
C25	0.167(1)	0.753(1)	0.374(1)	5.0(3)
C26	0.211(1)	0.7986(9)	0.2676(9)	3.9(2)
Zn2	0.500	0.500	0.0000	2.47(3)
O2	0.4571(7)	0.3411(5)	0.0790(6)	3.4(1)
N2	0.2744(8)	0.5801(6)	0.0101(7)	3.1(2)
N31	0.4078(8)	0.4869(6)	-0.1606(7)	3.0(2)
C3	0.221(1)	0.6359(9)	-0.1083(9)	3.8(2)
C4	0.191(1)	0.4910(9)	0.063(1)	3.9(2)
C32	0.293(1)	0.5583(8)	-0.1924(9)	3.3(2)
C33	0.227(1)	0.575(1)	-0.300(1)	4.7(3)
C34	0.295(1)	0.511(1)	-0.376(1)	5.1(3)
C35	0.417(2)	0.436(1)	-0.3451(9)	5.5(3)
C36	0.482(1)	0.4197(9)	-0.2356(9)	4.1(2)
C41	0.383(1)	0.3508(8)	0.1748(9)	3.5(2)
C42	0.255(1)	0.4248(8)	0.1736(9)	3.5(2)
C43	0.184(1)	0.438(1)	0.275(1)	5.8(3)
C44	0.243(2)	0.375(1)	0.377(1)	6.2(3)
C45	0.370(2)	0.300(1)	0.381(1)	7.1(3)
C46	0.446(1)	0.283(1)	0.280(1)	5.0(3)
Ow1	0.4355(8)	0.8483(6)	0.0006(7)	4.7(2)
Ow2	0.4246(9)	0.0562(8)	0.8473(8)	5.7(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) + bc(\cos \alpha) * B(2,3)]$.

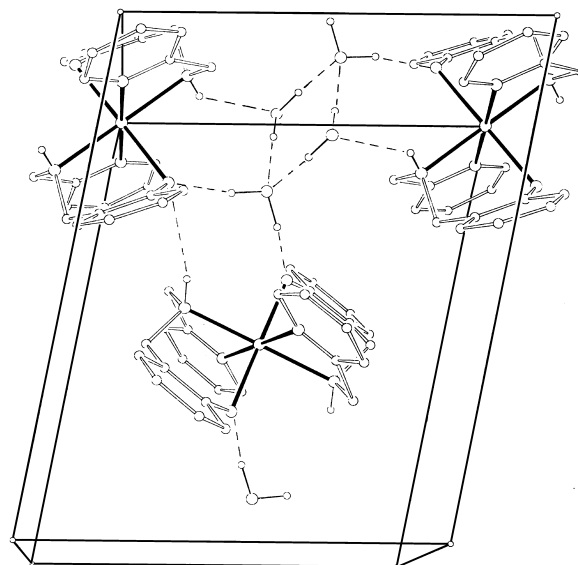
**Figure 2.** ORTEP of the molecule 1, showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted.

The molecular structure of each molecule in **1** shows two deprotonated bpa⁻ ligands facially coordinated to the Zn²⁺ ion through the nitrogen (amine and pyridine) and oxygen (phenolate) donors. Since the molecules possess inversion centers, atoms of the same nature (two N_{amine}, two N_{pyridine}, and two O_{phenolate}) must be coordinated in *trans* positions with respect to each other. The six-membered chelate rings (ZnONC₃) adopt chair conformations with the torsion angles N1-C2-C22-C21 of -67(1)° and N2-C4-C42-C41 of -69(1)°. The remaining five-membered rings formed by the 2-pyridylmethyl groups are rigid and deviate slightly from planarity, with the sum of the interior angles being 526° and 527° for Zn1-N1-C1-C12-N11 and Zn2-N2-C3-C32-N31 rings, respectively. The angles N1-Zn1-N11 = 79.7(3)° in molecule 1 and N2-Zn2-N31 = 76.4(3)° in molecule 2 are significantly smaller than the ideal octahedral angle of 90° and are a reflection of the rigidity of these five-membered rings. The torsion angles N11-Zn1-N1-C1 = 30.0(6)° and Zn1-N11-C12-C1 = 1.5(9)°, and N31-Zn2-N2-C3 = 31.5(6)° and Zn2-N31-C32-C3 = 7.6(9)° give us the extent of puckering in the outer and inner regions of molecules 1 and 2, respectively. The Zn-Namine bond lengths of 2.148(8) Å in molecule 1 and

Table 2. Bond lengths (Å), with e.s.d's in parentheses.

Molecule 1			Molecule 2		
Zn1	O1	2.154(6)	Zn2	O2	2.076(6)
Zn1	N1	2.148(8)	Zn2	N2	2.186(7)
Zn1	N11	2.160(8)	Zn2	N31	2.167(8)
O1	C21	1.32(1)	O2	C41	1.35(1)
N1	C1	1.47(1)	N2	C3	1.50(1)
N1	C2	1.47(1)	N2	C4	1.50(1)
N11	C12	1.35(1)	N31	C32	1.26(1)
N11	C16	1.33(1)	N31	C36	1.41(1)
C1	C12	1.51(1)	C3	C32	1.56(1)
C2	C22	1.51(2)	C4	C42	1.48(1)
C12	C13	1.40(2)	C32	C33	1.41(2)
C13	C14	1.39(2)	C33	C34	1.37(2)
C14	C15	1.35(2)	C34	C35	1.34(2)
C15	C16	1.37(2)	C35	C36	1.42(2)
C21	C22	1.40(1)	C41	C42	1.36(1)
C21	C26	1.41(2)	C41	C42	1.36(1)
C22	C23	1.41(2)	C42	C43	1.40(2)
C23	C24	1.36(2)	C43	C44	1.38(2)
C24	C25	1.37(2)	C44	C45	1.36(2)
C25	C26	1.39(2)	C45	C46	1.42(2)

2.186(7) Å in molecule 2 compare very well with the corresponding distances observed in the centrosymmetric pseudo-octahedral structure of the $[\text{ZnL}_2](\text{PF}_6)_2$ complex (L = 1,4,7-triazacyclononane), which are in the range of 2.156(5) to 2.187(5) Å¹⁶, while the $\text{Zn1-N}_{\text{pyridine}} = 2.160(8)$ Å and $\text{Zn2-N}_{\text{pyridine}} = 2.167(8)$ Å are in good agreement with the $\text{Zn-N}_{\text{pyridine}}$ bonds (average = 2.170 Å detected in $[\text{Zn}(\text{bpy})_3](\text{ClO}_4)_2$ ¹⁷). However, these distances are significantly longer than those observed in the equatorial plane ($\text{Cu-N}_{\text{amine}} = 2.003$ Å and $\text{Cu-N}_{\text{pyridine}} = 2.051$ Å) of the $[\text{Cu}(\text{Hbpa})_2]^{2+}$ complex, which has a similar arrangement of the Hbpa ligand around the Cu^{2+} ¹⁸. This may arise from the presence of cationic species in the Cu^{2+} complex, compared with the neutral complex **1**. From this point of view it is consistent to consider a decrease of electron density at the Cu^{2+} center, that determines an increase of the Cu-N bond order, and consequently the shortening of the $\text{Cu-N}_{\text{amine}}$ and $\text{Cu-N}_{\text{pyridine}}$ bond lengths. It is important to note that the ionic radii of Cu^{2+} and Zn^{2+} with O_h symmetry are similar, at 87 and 88 pm, respectively¹⁹. The $\text{Zn-O}_{\text{phenolate}}$ bonds in molecules 1 and 2 are very

**Figure 3.** Packing diagram viewed down the *c* axis (*a* horizontal). Hydrogen bonds are shown by dashed lines. All atoms are represented by spheres of arbitrary radii.

different with $\text{Zn1-O1} = 2.154(6)$ Å and $\text{Zn2-O2} = 2.076(6)$, and are a consequence of the distinct hydrogen contacts of the O1 and O2 atoms. Details of the hydrogen bonding scheme are in Table 4. The crystal structure is shown in projection down the *c* axis with the hydrogen bonds (Fig. 3). On the other hand, these bonds are significantly longer than those generally found in the equatorial plane of trigonal bipyramidal complexes, which fall in the range of 1.9–2.0 Å. This unusual structural feature can be tentatively explained as a result of a mutual *trans* effect caused by the phenolate groups which are coordinated in *trans* positions with respect to each other. Unfortunately, the lack of structural data for octahedral zinc-phenolate complexes restrict us from further comparisons. Indeed, to the best of our knowledge, $[\text{Zn}(\text{bpa})_2] \cdot 2\text{H}_2\text{O}$ is the first structural example of an octahedral Zn^{2+} complex which contains phenolate in its coordination sphere.

Finally, we conclude that some appropriate synthetic modifications of **1** are necessary to obtain more adequate models for astacin. The synthesis of analogues of **1** in which one or two phenolates could be protonated are in progress in our laboratory and will be the subject of future reports. This has already been achieved with the corresponding copper complex¹⁸.

Supplementary Material

The list of observed and calculated structural factors, anisotropic temperature factors, and hydrogen coordinates are available from the authors (I.V.) upon request.

Acknowledgments

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Table 3. Bond angles ($^{\circ}$), with e.s.d.'s in parentheses.

O1	Zn1	N1	88.4(3)	O2	Zn2	N2	90.5(3)
O1	Zn1	N11	89.2(3)	O2	Zn2	N31	92.3(3)
N1	Zn1	N11	79.7(3)	N2	Zn2	N31	76.4(3)
Zn1	O1	C21	109.3(5)	Zn2	O2	C41	110.9(6)
Zn1	N1	C1	105.6(6)	Zn2	N2	C3	107.7(6)
Zn1	N1	C2	112.4(6)	Zn2	N2	C4	110.0(5)
C1	N1	C2	112.0(8)	C3	N2	C4	111.9(8)
Zn1	N11	C12	111.3(8)	Zn2	N31	C32	115.6(7)
Zn1	N11	C16	128.8(8)	Zn2	N31	C36	122.6(6)
C12	N11	C16	119.5(9)	C32	N31	C36	120.7(9)
N1	C1	C12	112.6(8)	N2	C3	C32	108.6(7)
N1	C2	C22	113.4(9)	N2	C4	C42	112.1(9)
N11	C12	C1	117.7(8)	N31	C32	C3	118.4(9)
N11	C12	C13	120.7(8)	N31	C32	C33	125(1)
C1	C12	C13	122(1)	C3	C32	C33	116.9(8)
C12	C13	C14	119(1)	C32	C33	C34	117(1)
C13	C14	C15	119(1)	C33	C34	C35	120(1)
C14	C15	C16	120(1)	C34	C35	C36	122(1)
N11	C16	C15	122(1)	N31	C36	C35	115.5(9)
O1	C21	C22	119.9(9)	O2	C41	C42	121.8(8)
O1	C21	C26	121.8(9)	O2	C41	C46	117.5(9)
C22	C21	C26	118.3(9)	C42	C41	C46	121(1)
C2	C22	C21	117.9(9)	C4	C42	C41	119.0(9)
C2	C22	C23	122(1)	C4	C42	C43	120.3(9)
C21	C22	C23	120(1)	C41	C42	C43	120.7(9)
C22	C23	C24	120(1)	C42	C43	C44	120(1)
C23	C24	C25	120(1)	C43	C44	C45	121(1)
C24	C25	C26	121(1)	C44	C45	C46	122(1)
C21	C26	C25	120(1)	C41	C46	C45	117(1)

Table 4. Hydrogen-bonding geometry (\AA , $^{\circ}$).

D - H...A	D... A	D-H	H...A	D-H...A
Ow1 - H1w1..O2 ⁱ	2.64(1)	1.04	1.61	172
Ow1 - H2w1..O1	2.70(1)	1.00	1.71	167
Ow2 - H1w2..Ow1 ⁱⁱ	2.80(1)	0.98	1.82	173
Ow2 - H2w2..Ow1 ⁱⁱⁱ	2.78(1)	0.98	1.82	168
N1 - H1n..Ow2 ^{iv}	2.99(1)	0.95	2.08	160
N2 - H2n..O1	3.42(1)	0.95	2.59	146

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