

Synthesis and Characterization of the Novel Tetraazadiphenol Macrocyclic Dicopper(II) Complex Containing Chelate Nitrite Ligands

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Interest in the synthesis of new tetraazadiphenol macrocyclic dicopper(II) complexes is mainly due to their applications in bioinorganic chemistry,¹ magnetochemistry² and homogeneous catalysis.³ The metal ions present in naturally occurring systems are involved in the biochemical reactions. There has been considerable interest in nitrite complexes of Cu(II) owing to the nitrite-reductase roles of copper-containing enzymes.⁴ The ambidentate NO₂⁻ ligand is known to coordinate to nitrogen or to oxygen in metal complexes. The NO₂⁻ ion can behave as a monodentate ligand *via* either nitrogen or oxygen. As a bidentate ligand, it can chelate or bridge *via* nitrogen and oxygen or *via* a single oxygen atom.⁵

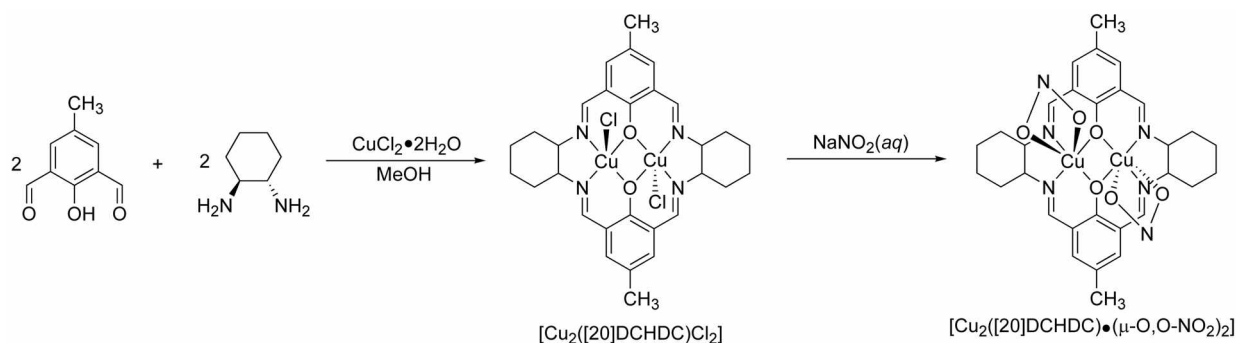
Recently we have reported the first tetraazadiphenol macrocyclic mononuclear nickel(II) complex [Ni(H₂[20]-DCHDC)](ClO₄)₂ {H₂[20]-DCHDC = 14,29-dimethyl-3,10,18,25-tetraazapentacyclo-[25.3.1.0^{4,9}.1^{12,16}.0^{19,24}]dtriacontane-2,10,12,14,16(32),17,27(31),28,30-decane-31,32-diol} based on chiral diamine skeletons.⁶ Schiff base macrocycles containing two bridging phenol groups have been widely used to synthesize homo- and hetero-multinuclear transition metal complexes.⁷ Most investigations of these 3*d*-metal ion complexes are an outgrowth of stereoselective catalysts in reactions such as alkene epoxidation,⁸ epoxide carboxylation,⁹ intramolecular reductive cyclization,¹⁰ electrochemical annulation,¹¹ and oxidation of hydrocarbons.¹² All of these processes can potentially generate stereogenic centers, thus the chiral macrocycles, which can induce chirality, are of great interest.

"Robson" type macrocyclic complexes, formed by 3*d*-metal ion template condensation of 2,6-diformyl-*p*-cresols (DFPC) and achiral alkylenediamines, contain phenoxide

oxygen atoms bridging the two 3*d*-metal centers and represent ideal systems to examine the exchange coupling *via* phenoxide oxygen.^{6,13} When a chiral diamine is used in the template reaction with 2,6-diformylpyridine, chiral complexes can be obtained. In the case of the chiral precursor (1*R*, 2*R*)-1,2-diaminocyclohexane, enantiopure lanthanide(III) complexes [LnL_{m1}]₃·*n*H₂O (where Ln, L_{m1} and X exhibit the lanthanide(III) ion, macrocycle and monoanion, respectively) are formed.¹⁴ The structures and chemical properties of these complexes are affected by various types of the axial ligands.¹⁵ It is found that the crystal structure of the nitrito nickel(II) complex with macrocyclic ligand (L_{m2} = 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane) reveals a six-coordinated bicapped square-pyramidal geometry. This result contrasts with other reports in which the coordination geometries around nickel(II) ions in tetraaza macrocyclic complexes are known to be usually an axially elongated octahedral or square-pyramidal arrangement with bonds to auxiliary ligand.¹⁶ In order to better understand some aspects of different molecular topologies, we report herein the synthesis, properties and crystal structure of tetraazadiphenol macrocyclic dinuclear copper(II) complex [Cu₂([20]-DCHDC)(O₂N)₂]·6H₂O (**II**), which is prepared by reaction of [Cu₂([20]-DCHDC)Cl₂]·H₂O (**I**) with NaNO₂, as depicted in Scheme 1. The dinuclear Cu(II) chloro complex **I** is synthesized by mixing DFPC and chiral precursor (1*R*, 2*R*)-1,2-diaminocyclohexane.⁶

Experimental Section

General methods. All chemicals were commercial analy-



Scheme 1. Synthetic route of the dinuclear tetraazadiphenol macrocyclic copper(II) complexes.

tical reagents and were used without further purification. Solvents used for electrochemical and spectroscopic studies were purified by standard procedures. DFPC was prepared with high yields by an improved oxidation method using active manganese(IV) dioxide.¹⁷

Microanalyses of C, H, and N were carried out using LECO CHN-900 analyzer. Conductance measurements of the complexes were performed in CH₃OH or DMSO at 25 ± 1 °C using an ORION 162 conductivity temperature meter. IR spectra were recorded with a Bruker FSS66 FT-IR spectrometer. FAB-MS spectra were obtained on a JEOL JMS-700 Mass Spectrometer using argon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and glycerol was used as the matrix. The mass spectrometer was operated in positive ion mode and mass spectra were calibrated by Alkali-CsI positive.

Synthesis of [Cu₂([20]-DCHDC)Cl₂·H₂O (I). A methanolic solution (50 mL) of 2,6-diformyl-*p*-cresol (3.280 g, 20 mmol) was added to a suspension of the trans-1,2-diaminocyclohexane (2.400 g, 20 mmol) and cupric chloride dehydrate (3.410 g, 20 mmol) in methanol (30 mL). The mixture was refluxed for 2 h, forming a deep blue solution. The solution was concentrated until a dark precipitates were just resulted. Tetrahydrofuran (200 mL) was added to the mixture, and the resulted pale green products were filtered, thoroughly washed with water, and dried at 150 °C *in vacuo*. Yield: 64%. Anal. Calcd (Found) % for C₃₀H₃₆N₄O₃Cl₂Cu₂: C, 51.58 (51.62); H, 5.19 (5.01); N, 8.02 (8.15). λ_M (methanol): 65 ohm⁻¹cm²mol⁻¹.

Synthesis of [Cu₂([20]-DCHDC)(O₂N)₂·6H₂O (II). To an aqueous solution (150 mL) of [Cu₂([20]-DCHDC)Cl₂·H₂O (0.6986 g, 1 mmol), sodium nitrite (0.3450 g, 5 mmol) in water (20 mL) was added dropwise with stirring. The resulting mixture was refluxed for 2 h, then evaporated under reduced pressure until a green precipitate separated. This was collected by filtration, thoroughly washed with water, and dried *in vacuo*. Yield 83%. Anal. Calcd (Found) % for C₃₀H₃₆N₆O₁₂Cu₂: C, 44.50 (44.18); H, 5.73 (5.46); N, 10.38 (9.44). λ_M (methanol): 66 ohm⁻¹cm²mol⁻¹.

X-ray crystallography of complex. Crystals of **II** suitable for X-ray diffraction study were grown from 10:1 mixture of methanol and water of **II** over a week at room temperature. The green colored single crystal of complex was attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Crystal structure was solved by the direct methods¹⁸ and refined by full-matrix least-squares method by using the SHELXL program of the SHELXTL package,¹⁹ with 2078 of 10154 unique reflections measured. The intensity data were corrected for Lorentz and polarization effects during data reduction. All non-hydrogens atoms of the copper(II) complex were refined on *F*² by the full matrix least-squares procedure using anisotropic displacement parameters. Hydrogen atoms were generated geometrically, assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic *U* of the atoms to which they are attached [*U*_{iso} = 1.2*U*_{eq} (parent

Table 1. Crystal data and details of the structure determination for complex **II**

Empirical formula	C ₃₀ H ₃₆ N ₆ O ₁₂ Cu ₂
Temperature, K	173(2)
Crystal system, Space group	Orthorhombic, <i>Cmca</i>
<i>a</i> , Å	16.9119(12)
<i>b</i> , Å	8.0883(6)
<i>c</i> , Å	24.5802(17)
<i>Z</i>	4
Density (calculated), g/cm ³	1.600
Absorption coefficient, mm ⁻¹	1.337
<i>F</i> (000)	1688
Theta range for data collection, °	1.66 to 28.28.
Reflections collected	10154
Independent reflections	2078 [<i>R</i> (int) = 0.0614]
Goodness-of-fit on <i>F</i> ²	1.071
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0457, <i>wR</i> ₂ = 0.1291
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0557, <i>wR</i> ₂ = 0.1413

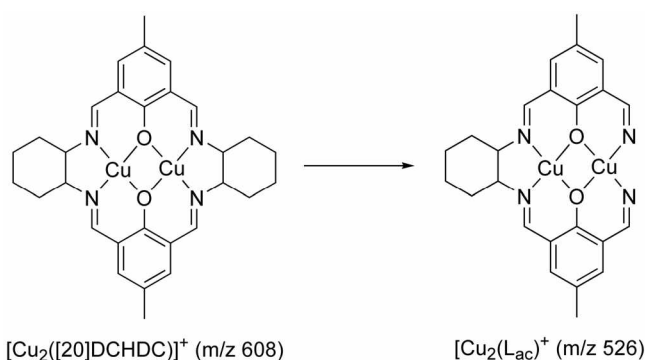
$$R = \sum |F_o - |F_c|| / \sum |F_o|, R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}, w = 1 / [\sigma^2(F_o^2) + (0.0791P)^2 + 5.7782P] \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

atom]) and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for complex **II** is described in Table 1.

Results and Discussion

General properties. The complexes **I** and **II** are soluble in methanol, chloroform, DMSO and water. The molar conductance (λ_{M(methanol)} = 65 ohm⁻¹cm²mol⁻¹) of complexes **I** and **II** is consistent with a non-electrolytic behavior. The visible spectrum of chloro complex **I** shows a characteristic band near 650 nm. In general typical Cu(II) complexes of square pyramidal(SP) or distorted SP geometries exhibit a band in the 550-650 nm range.²⁰ Complex **II** displayed a broad band centered at 530 nm arising from ²E_g → ²T_{2g} (*O_h*) transition, showing the characteristic feature of Jahn-Teller effects of Cu(II) ions. The formation of dinuclear Cu(II) complexes, inferable from elemental analyses, molar conductances and electronic absorption spectra of the **I** and **II**, is evidenced by characteristic IR absorption bands and FAB mass spectra. For complex **II**, strong evidence that aldehyde groups had been completely converted into Schiff base residues was provided by the disappearance of the aldehydic C=O stretching band at 1627 cm⁻¹ and the appearance of a strong band at 1624-1635 cm⁻¹ assigned to ν(C=N) stretching band. The bands that appear near 3000-2800 cm⁻¹ and 1550 cm⁻¹ are due to C-H and aromatic ring C=C stretching vibrations, respectively. The sharp absorption bands near 1240 cm⁻¹ are attributed to phenolic C-O vibration. The most relevant feature of the IR spectrum in **II** is the evidence for the chelating nitrito coordination. The IR spectrum of the nitrito group in **II** appears at 1446 cm⁻¹ and 1205 cm⁻¹ corresponding to the asymmetric and symmetric -ONO stretching vibrations, respectively, which is consistent with the crystal structure.²¹

The significant ions observed in the FAB mass spectrum



Scheme 2. Assignment of the mass spectrum of $[\text{Cu}_2([\text{20}]\text{DCHDC})(\text{NO}_2)_2]^+$.

of complex **I** include $[\text{Cu}_2(\text{L}_{\text{bac}})]^+$ (structure proposed in Scheme 2), $[\text{Cu}([\text{20}]\text{-DCHDC})]^+$, $[\text{Cu}_2([\text{20}]\text{-DCHDC})]^+$ and $[\text{Cu}_2([\text{20}]\text{-DCHDC})\text{Cl}]^-$, at m/z 526, 545, 608 and 643, respectively. The mass spectrum of **II** shows three major fragments centered around m/z 608, 526 and 545, which are ascribed to the $[\text{Cu}_2([\text{20}]\text{-DCHDC})]^+$, $[\text{Cu}_2(\text{L}_{\text{bac}})]^+$ (structure proposed in Scheme 2) and $[\text{Cu}([\text{20}]\text{-DCHDC})]^+$, respectively, a result that strongly supports the presence of dinuclear active sites in the macrocyclic complex. On the contrary the complex **II** acyclic fragment ion ($[\text{Cu}_2(\text{L}_{\text{bac}})]^+$) was detected with significant abundance, macrocycle $\text{H}_2[\text{20}]\text{-DCHDC}$ or $\text{H}_2[\text{22}]\text{-HMTADO}$ leaves intact in the complexes $[\text{Ni}(\text{H}_2[\text{20}]\text{-DCHDC})(\text{ClO}_4)_2]$, $[\text{Ni}_2([\text{22}]\text{-HMTADO})(\text{CN})_2] \cdot 0.5\text{H}_2\text{O}$, $[\text{Ni}_2([\text{22}]\text{-HMTADO})(\mu\text{-O}_2\text{N})(\text{NO}_2)(\text{OH}_2)]$, $[\text{Cu}_2([\text{22}]\text{-HMTADO})(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 10\text{H}_2\text{O}$.^{6,13(b)} We observe that in these complexes macrocycle is more stable than that of the complex **I** and **II** under the conditions of this analysis. These major peaks are associated with peaks of mass one or two greater or less, which are attributed to protonated/deprotonated forms.

Description of crystal structure. The crystal **II** crystallizes in the orthorhombic space group $Cmca$ with $a = 16.9119(12)$ Å, $b = 8.0883(6)$ Å, $c = 24.5802(17)$ Å, and $\beta = 90^\circ$. The crystal structure of complex **II** is made up of a

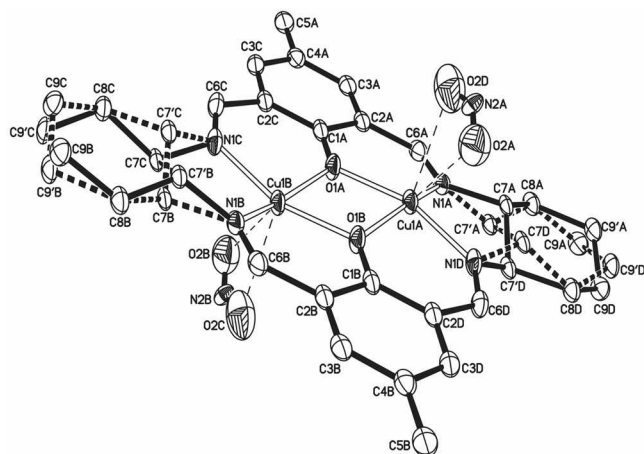


Figure 1. ORTEP representation of core structure (top view) and atom labeling scheme for $[\text{Cu}_2([\text{20}]\text{-DCHDC})(\text{O}_2\text{N})_2] \cdot 6\text{H}_2\text{O}$ showing 50% probability thermal ellipsoids.

Table 2. Selected bond lengths (Å) and angles ($^\circ$) for $[\text{Cu}_2([\text{20}]\text{-DCHDC})(\text{O}_2\text{N})_2] \cdot 6\text{H}_2\text{O}$

Cu(1)-N(1)	1.903(2)	Cu(1)-O(2)	2.614(5)
Cu(1)-N(1) ^{#1}	1.903(2)	Cu(1)-Cu(1) ^{#2}	2.954(8)
Cu(1)-O(1) ^{#2}	1.912(2)	O(1)-Cu(1) ^{#2}	1.912(2)
Cu(1)-O(1)	1.912(2)	N(2)-O(2)	1.038(6)
N(1)-Cu(1)-N(1) ^{#1}	88.75(14)	N(1) ^{#1} -Cu(1)-Cu(1) ^{#2}	129.99(7)
N(1)-Cu(1)-O(1) ^{#2}	160.15(8)	O(1) ^{#2} -Cu(1)-Cu(1) ^{#2}	39.41(7)
N(1) ^{#1} -Cu(1)-O(1) ^{#2}	93.01(10)	O(1)-Cu(1)-Cu(1) ^{#2}	39.41(7)
N(1)-Cu(1)-O(1)	93.01(10)	O(2)-Cu(1)-Cu(1) ^{#2}	104.51(8)
N(1) ^{#1} -Cu(1)-O(1)	160.15(8)	C(1)-O(1)-Cu(1) ^{#2}	129.41(7)
O(1) ^{#2} -Cu(1)-O(1)	78.82(14)	C(1)-O(1)-Cu(1)	129.41(7)
N(1)-Cu(1)-O(2)	112.32(12)	Cu(1) ^{#2} -O(1)-Cu(1)	101.18(14)
N(1) ^{#1} -Cu(1)-O(2)	81.76(13)	C(6)-N(1)-Cu(1)	125.54(18)
O(1) ^{#2} -Cu(1)-O(2)	87.49(11)	C(7)-N(1)-Cu(1)	111.8(3)
O(1)-Cu(1)-O(2)	115.54(10)	N(2)-O(2)-Cu(1)	87.2(4)
N(1)-Cu(1)-Cu(1) ^{#2}	129.99(7)	O(2) ^{#1} -N(2)-O(2)	140.9(7)

Symmetry transformations used to generate equivalent atoms: ^{#1} -x, y, z; ^{#2} -x, -y, -z - 1

neutral $[\text{Cu}_2([\text{20}]\text{-DCHDC})(\text{O}_2\text{N})_2]$ unit. An ORTEP view of this complex is shown in Figure 1 together with the numbering scheme. The dinuclear structure with two Cu(II) ions is centrosymmetry, which each copper(II) ion has a six-coordinated capped square-pyramidal geometry with the N_2O_2 -donor dinucleating macrocycle $[\text{20}]\text{-DCHDC}$ adopting a tetradentate ligand about the central metal and the remaining two coordination sites being occupied by a chelate nitrito (O, O') ligand in the approximately apical position. A chelate nitrito (O, O') complex **II** is expected since Cu(II) is normally considered a borderline ion that prefers O over N donors. To the best of our knowledge, complex **II** represents the first structurally characterized example of a macrocyclic dinuclear nitrito Cu(II) complex containing two bidentate nitrite ligands.

Selected bond lengths and angles relevant to the coordination geometries are listed in Table 2. The macrocyclic complex adopts a non-flat structure with the two capped pyramidal copper centers bridged by the two phenoxide oxygen atoms, with the angle Cu-O-Cu of $101.18(14)^\circ$ and Cu-Cu separation of $2.954(8)$ Å.²³ The basal Cu-ligand bond lengths fall in the range $1.903(2)$ - $1.912(2)$ Å, and two nitrite ions occupy apical positions in a trans arrangement with somewhat longer contacts {Cu-O(2) $2.614(5)$ Å} owing to the Jahn-Teller effect in d^9 electronic configuration. Both the copper centers are displaced toward the nitrite ions by 0.3288 Å from the mean N_2O_2 basal plane. Interestingly, $\eta^2\text{-NO}_2$ coordination of complex **II** is less common because of the steric hindrance caused by cyclohexane groups of the macrocycle compared with analogous open-chain ligands. The bond angles $\text{N}(1)\text{-Cu}(1)\text{-N}(1)^{\#1}$, $\text{N}(1)\text{-Cu}(1)\text{-O}(1)^{\#2}$, $\text{O}(1)^{\#2}\text{-Cu}(1)\text{-O}(1)$ and $\text{N}(1)^{\#1}\text{-Cu}(1)\text{-O}(2)$ are $88.75(14)$, $160.15(8)$, $78.82(14)$ and $81.76(13)^\circ$, respectively.

As shown in Figure 2 there are two kinds of an intermolecular hydrogen bonding in complex **II**. Hydrogen bonds in the macrocyclic binuclear complexes play the pivotal role in crystal packing and non-covalent framework structure in supramolecular chemistry.²³ The oxygen atom of nitrite ion

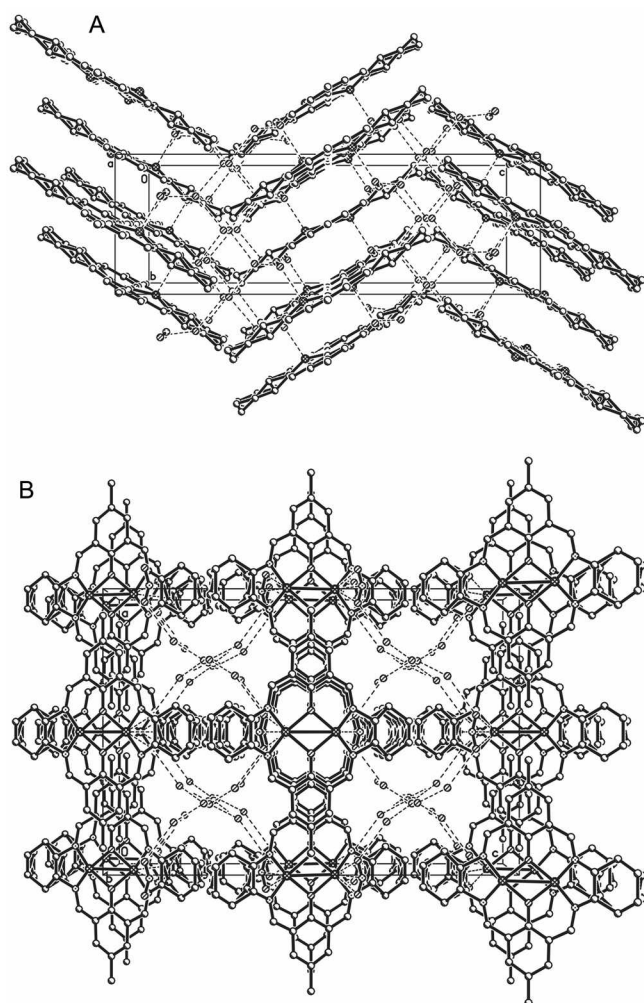


Figure 2. The a-axis (A) and b-axis (B) projections of the molecular packing present in $[\text{Cu}_2([\text{20-DCHDC})(\text{O}_2\text{N})_2] \cdot 6\text{H}_2\text{O}$ containing hydrogen bonding.

is hydrogen bonded with the adjacent water $\{\text{Ow}(2) \cdots \text{O}(2)$ Å: 2.812 Å. $\text{Ow}(2)\text{-Hw}(2\text{B}) \cdots \text{O}(2)$: 149.37° . Hydrogen bonds of the type $\text{Ow-H} \cdots \text{Ow}$ between water molecules are simultaneously observed in the investigating complex $\{\text{Symmetry code } (x, -y, -z + 1) \text{Ow}(1) \cdots \text{Ow}(2)$: 2.985 Å. $\text{Ow}(1)\text{-Hw}(1) \cdots \text{Ow}(2)$: 137.10° . Symmetry code $(x, -y + 1/2, z + 1/2) \text{Ow}(2) \cdots \text{Ow}(1)$: 2.751 Å. $\text{Ow}(2)\text{-Hw}(2\text{A})\text{O} \cdots \text{w}(1)$: 168.40° . Symmetry code $(-x + 1/2, -y + 1/2, -z + 1) \text{Ow}(2) \cdots \text{Ow}(1)$: 2.942 Å. $\text{Ow}(2)\text{-Hw}(2\text{A}) \cdots \text{Ow}(1)$: 166.72° .

Supplementary material. Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Center. CCDC number 285723. The data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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