

## Sodium templated formation of a unique tetradecanuclear $\{Zn_{12}(\mu_3-OH)_6Na_2(\mu_2-O)\}^{18+}$ hetero-metal cluster core having an auxiliary bithiazole dibenzoate ligand



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### ABSTRACT

A three-dimensional (3D) metal-organic framework having a unique tetradecanuclear  $\{Zn_{12}(\mu_3-OH)_6Na_2(\mu_2-O)\}^{18+}$  hetero-metal cluster core, formulated as  $\{Zn_{12}(BTDA)_9(\mu_3-OH)_6Na_2(\mu_2-O)\}$  (**1**) [ $H_2BTDA = 4,4'-(4,4'-dibutyl-2,2'-bithiazole-5,5'-diyl)dibenzoic$  acid], has been described herein. The tetradecanuclear hetero-metal cluster core is composed of two heptanuclear  $\{Zn_6(\mu_3-OH)_3Na\}^{10+}$  trifolium-shaped subunits where the axle sodium(I) ion is connected with three pairs of zinc(II) ions by three  $\mu_3-OH$  ions and the two sodium(I) ions are further linked by a  $\mu_2-oxo$  bridge. Besides, the auxiliary BTDA ligand serves as a multi-dentate bridging mode linking adjacent tetradecanuclear hetero-metal clusters into a 3D coordination polymer where a rhombohedral array with a new  $(4^{18} \cdot 8^{108} \cdot 12^{27}) \cdot (4)_9$  topology is observed.

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Research on the metal-organic frameworks (MOFs) has attracted considerable attention in the field of molecule-based materials in recent years [1–3]. Recently, the syntheses and assemblies of versatile MOFs have a rocketed growth in coordination chemistry and crystal engineering, not only because of their various and intriguing molecular structures, but also owing to their interesting optical, electronic, ferroelectric, catalytic and magnetic properties [4–8]. One of the most important problems is how to design and select suitable organic functional building blocks with fixed geometry and variable coordination modes in order to rationally produce MOFs on the basis of self-assembly [9,10]. In addition, the presence of suitable metal ions is vital in constituting certain functional MOFs. For example, many high-performance luminescent materials have been reported, where simple  $d^{10}$  metal ions, such as Cu(I), Ag(I), Zn(II) and Cd(II), are commonly involved [11,12]. However, metal clusters can also serve as the nodes instead of simple metal ions to produce fluorescent MOFs. Compared with the simple metal ions, the metal clusters have the advantage to hold more directional information by predestined bridging ligands, and then to control the overall coordination networks [13].

Based upon the above-mentioned considerations, we think 4,4'-(4,4'-dibutyl-2,2'-bithiazole-5,5'-diyl)dibenzoic acid ( $H_2BTDA$ ) is a good candidate for assembling luminescent MOFs because its large  $\pi$ -conjugated aromatic heterocyclic system can afford both ligand based luminescence and ligand-to-metal (or metal-to-ligand) charge transfer based luminescence [14,15]. Besides, it is a multi-dentate chelating

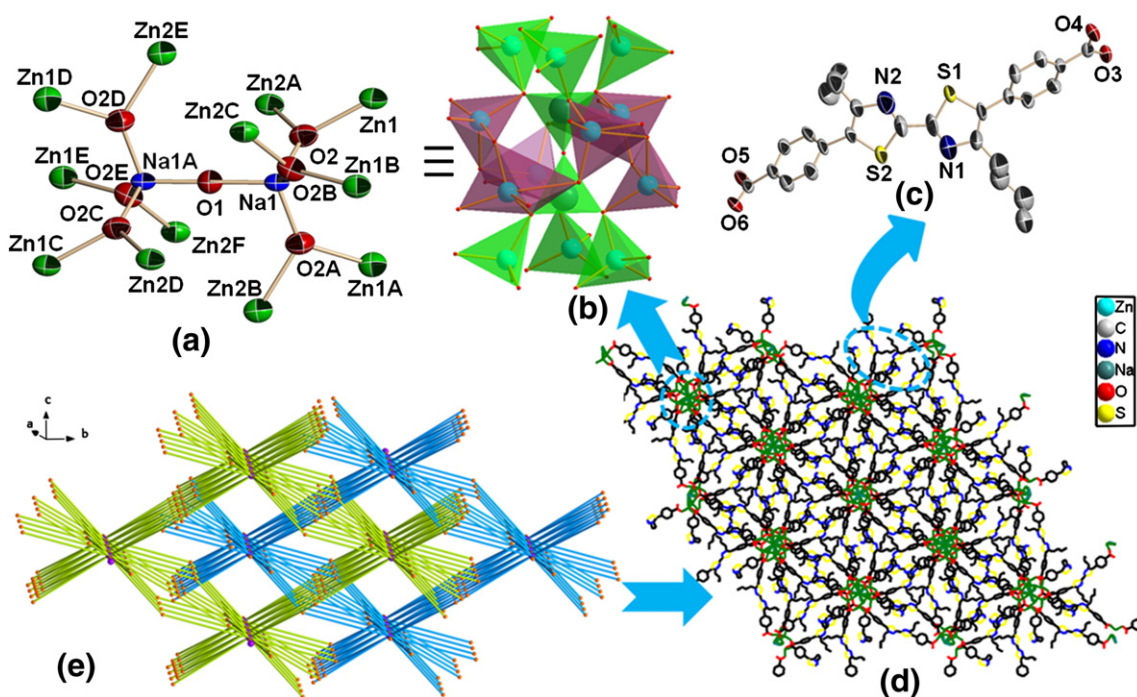
ligand in the deprotonated form which can link different metal ions to form rigid polymeric frameworks. In our previous work, we have described a series of coplanar bithiazole-centered heterocyclic aromatic fluorescent compounds having different donor/acceptor terminal groups including the single-crystal structure of  $H_2BTDA$  [16]. However, BTDA-based metal complexes have not been reported up until now.

Herein, we report the synthesis [17] and single-crystal structure [18] of a new 3D zinc(II)/Na(I) hetero-metal coordination polymer formulated as  $\{Zn_{12}(BTDA)_9(\mu_3-OH)_6Na_2(\mu_2-O)\}$  (**1**). Our synthetic strategy is based on the sodium templated method, in which the starting material  $H_2BTDA$  was prepared according to the previously reported approaches [16]. A solvothermal reaction of  $Zn(ClO_4)_2 \cdot 6H_2O$ ,  $H_2BTDA$  and NaOH in a mole ratio of 1:1:2 in EtOH (10 mL) sealed in a 20 mL Teflon lined stainless steel autoclave yields complex **1** at 120 °C for 3 days, where the  $Na^+$  ion in this case acts as a template indeed in the self-assembly of the tetradecanuclear hetero-metal cluster.

The molecular structure of **1** with the atom-numbering schemes is shown in Fig. 1, and the selected bond distances and bond angles are listed in Table 1. As shown in Fig. 1a, it has a unique tetradecanuclear  $\{Zn_{12}(\mu_3-OH)_6Na_2(\mu_2-O)\}^{18+}$  hetero-metal cluster core where two heptanuclear trifolium-shaped  $\{Zn_6(\mu_3-OH)_3Na\}^{10+}$  subunits are bridged by one  $\mu_2-oxo$  linkage with the  $\mu_2-O-Na$  bond length of 1.645(5) Å. The tetradecanuclear  $\{Zn_{12}(\mu_3-OH)_6Na_2(\mu_2-O)\}^{18+}$  unit consists of two four-coordinate sodium(I) ions, six four-coordinate and six five-coordinate zinc(II) ions where every  $OH^-$  group links adjacent two zinc(II) and one sodium(I) ions in a  $\mu_3$  fashion, as can be seen in Fig. 1b. The coordination geometry of two central Na(I) ions is slightly distorted tetrahedral, where four oxygen atoms from one  $\mu_2-O$  and

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**Fig. 1.** (a) ORTEP view of the tetradecanuclear  $\{Zn_{12}(\mu_3-OH)_6Na_2(\mu_2-O)\}^{18+}$  cluster core in **1**; (b) The coordination geometry of  $Zn^{II}$  and  $Na^I$  cations in **1**; (c) The molecular geometry of ligand BTDA as a subunit in **1**; (d) Crystal packing structure of **1**; (e) Perspective view of two-fold interpenetrating network in **1**, where hydrogen atoms are omitted for clarity.

three  $\mu_3$ -OH bridges occupy the coordination sites. The three symmetrically related  $\mu_3$ -OH-Na bond distances are longer (1.649(5) Å) than that of  $\mu_2$ -O-Na one, indicative of the right assignment of the OH<sup>-</sup> groups instead of the oxo units in this structure in addition to the charge equilibrium consideration. The coordination geometry of six four-coordinate Zn(II) ions is tetrahedral with the mean Zn-O coordinative bond length of 1.934(6) Å. In contrast, the coordination spheres for six five-coordinate Zn(II) ions are severely distorted trigonal bipyramidal ( $\tau = 0.596$ ) [19] due to the presence of a weak Zn-O coordinative bond (Zn2-O8 = 2.831(6) Å) and the mean Zn-O coordinative bond length for the other four is 1.947(6) Å.

It is noted that every tetradecanuclear cluster core cation in **1** is coordinated by thirty-six oxygen atoms from eighteen BTDA ligands. There are one and a half BTDA ligands in the asymmetric unit of **1** and they both have the *trans* configuration between each central  $\beta$ -substituted *n*-butyl thiazole ring. However, compared with the free H<sub>2</sub>BTDA molecule (Fig. 2a) [16], both of them show larger distortions

between the side benzene and the central bithiazole rings (44.8(3) – 60.3(3)° versus (33.3(5)°). As can be seen in Fig. 2b, the central two thiazole rings have a dihedral angle of 0° because of the presence of an inversion center in the middle, which is the same as the free ligand. Nevertheless, the dihedral angle between the side benzene and the central bithiazole rings is much higher at 60.1(4)°. In contrast, the other BTDA ligand (Fig. 2c) exhibits the dihedral angles of 10.7(5)° between each central thiazole ring and 60.3(3) and 44.8(3)° between the side benzene and the central bithiazole rings, respectively.

Every BTDA acts as a multi-dentate bridging ligand in **1** where all four oxygen atoms at each end of ligand BTDA link near zinc(II) centers belonging to two different tetradecanuclear  $\{Zn_{12}Na_2\}$  hetero-metal clusters. As depicted in Fig. 1d, a 3D network is constructed as a result where every tetradecanuclear cluster and nine BTDA ligands are alternately connected with a cluster-cluster (O1 ··· O1) separation of 24.323(1) Å forming a rhombohedral array of new  $(4^{18} \cdot 8^{108} \cdot 12^{27}) \cdot (4)_9$  topology (Fig. 1e). The  $\{Zn_{12}Na_2\}$  hetero-metal cluster can be regarded as the fusion of six-coordinate cage-like units, where the coordination environment of  $\{Zn_{12}Na_2\}$  cluster is octahedral and every three BTDA ligands occupies one vertex leading to a two-fold interpenetrating network rather than a cubic framework [20]. The remaining unoccupied space between the two interpenetrating rhombohedral  $\{Zn_{12}(BTDA)_9(\mu_3-OH)_6Na_2(\mu_2-O)\}_\infty$  network is occupied by two *n*-butyl chains on the  $\beta$ -position of each thiazole ring. As depicted in Fig. 1e, every three parallel linkers join neighboring two metal clusters, and every metal cluster is linked to six others. As an alternative way of comprehension, this structure can be further simplified into a pcu-type topology when only the connectivity between adjacent tetradecanuclear hetero-metal clusters is considered [21].

To further study the sodium template effect, the alterations of molar ratios and alkali metal ions have been carried out. The control experiments were performed by using LiOH, KOH as the metal sources and different molar ratios of three starting materials. However, powder X-ray diffraction (PXRD) and FT-IR spectral results demonstrate that those obtained powder samples are only impurities or even H<sub>2</sub>BTDA. That is to say, Li<sup>+</sup> and K<sup>+</sup> templated formation of similar hetero-metal cluster was not successful mainly because of the size effect [22] of alkali metal ions. That is to say, the ion size of Li<sup>+</sup> is too

**Table 1**  
Selected bond lengths (Å) and angles (°) for complex **1**.

| Bond distances           |          | Bond angles                          |          |
|--------------------------|----------|--------------------------------------|----------|
| Zn1–O2                   | 1.944(5) | O2–Zn1–O3                            | 113.5(2) |
| Zn1–O3                   | 1.902(6) | O2–Zn1–O4 <sup>a</sup>               | 106.0(2) |
| Zn1–O4 <sup>a</sup>      | 1.938(6) | O2–Zn1–O5 <sup>b</sup>               | 110.0(2) |
| Zn1–O5 <sup>b</sup>      | 1.953(6) | O3–Zn1–O4 <sup>a</sup>               | 119.6(3) |
| Zn2–O6                   | 1.952(6) | O3–Zn1–O5 <sup>b</sup>               | 108.5(3) |
| Zn2–O7                   | 1.936(5) | O4 <sup>a</sup> –Zn1–O5 <sup>b</sup> | 98.0(3)  |
| Zn2–O8 <sup>c</sup>      | 1.953(6) | O6–Zn2–O7                            | 104.9(3) |
| Zn2–O2 <sup>b</sup>      | 1.947(5) | O6–Zn2–O8 <sup>c</sup>               | 94.8(3)  |
| Na1–O1                   | 1.645(5) | O2 <sup>b</sup> –Zn2–O6              | 108.6(3) |
| Na1–O2 <sup>d</sup>      | 1.650(7) | O7–Zn2–O8 <sup>c</sup>               | 111.3(3) |
| Na1–O2                   | 1.649(6) | O2 <sup>b</sup> –Zn2–O7              | 114.1(2) |
| Zn1 ··· Zn1 <sup>d</sup> | 4.086(2) | O2 <sup>b</sup> –Zn2–O8 <sup>c</sup> | 120.2(2) |
| Zn2 ··· Zn2 <sup>e</sup> | 3.942(2) | O2–Na1–O2 <sup>a</sup>               | 110.2(2) |
| Zn2 ··· Na1 <sup>f</sup> | 4.242(4) | O2 <sup>d</sup> –Na1–O2 <sup>a</sup> | 110.2(2) |
| Zn2 ··· Na1 <sup>g</sup> | 3.212(1) | O1–Na1–O2                            | 108.8(3) |
| Na1 ··· Na1 <sup>h</sup> | 3.289(7) | Na1–O1–Na1 <sup>h</sup>              | 180      |

Symmetry codes: <sup>a</sup>, -x + y, 1-x, z; <sup>b</sup>, 1/3-x, 2/3-y, 5/3-z; <sup>c</sup>, x-y, x, 1-z; <sup>d</sup>, 1-y, 1 + x-y, z; <sup>e</sup>, y, -x + y, 1-z; <sup>f</sup>, -1/3 + x, -2/3 + y, -2/3 + z; <sup>g</sup>, 1/3 + x-y, -1/3 + x, 5/3-z; <sup>h</sup>, 2/3-x, 4/3-y, 7/3-z.

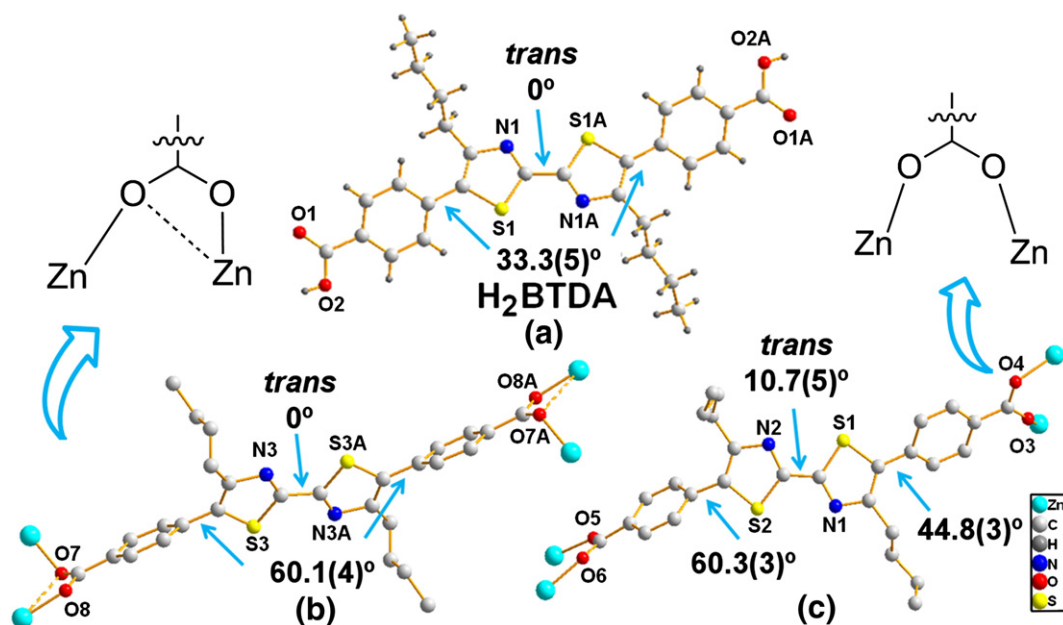


Fig. 2. Comparison between the free H<sub>2</sub>BTDA molecule (Upper) and the multi-dentate coordination fashions of BTDA ligand with the zinc(II) ions in **1** (Bottom) showing the dihedral angles and relative configurations between adjacent aromatic heterocycles.

small and the shape of K<sup>+</sup> is too big for this self-assembly reaction. In addition, BTDA ligand is suggested to play an important role in forming this 3D supramolecular framework.

The solid-state fluorescence spectra of H<sub>2</sub>BTDA and its hetero-metal complex **1** at room temperature are depicted in Fig. 3. Compared with 4,4'-dibutyl-2,2'-bithiazole, in which the fluorescence emission band is observed at  $\lambda_{\text{max}} = 389$  nm upon excitation at 350 nm, H<sub>2</sub>BTDA exhibits a strong yellow fluorescence emission peak at 458 nm upon excitation at the same wavelength [16]. The several tens of bathochromic shift for H<sub>2</sub>BTDA arises from the presence of a large conjugated  $\pi$ -system of the molecule. After the metal-ion complexation, different color luminescence is observed for **1**. Complex **1** displays two strong blue emission peaks at 366 and 386 nm with the excitation at 350 nm. The observation of blue-shifts in the solid-state fluorescence emission after metal-ion complexation is mainly because of the aforementioned distortions of adjacent aromatic ring in ligand BTDA (Fig. 2), which will reduce the planarity and the delocalization of conjugated  $\pi$ -system of the whole ligand.

In conclusion, a new 3D tetradecanuclear  $\{\text{Zn}_{12}(\mu_3\text{-OH})_6\text{Na}_2(\mu_2\text{-O})\}^{18+}$  hetero-metal cluster has been successfully synthesized by

using the sodium templated method. In complex **1**, two heptanuclear  $\{\text{Zn}_6(\mu_3\text{-OH})_3\text{Na}\}^{10+}$  trifolium-shaped subunits are found where the axle sodium(I) ion is connected with three pairs of zinc(II) ions by three  $\mu_3\text{-OH}$  ions and the two sodium(I) ions are further linked by a  $\mu_2\text{-oxo}$  bridge. The auxiliary BTDA ligand with a molecular length of 1.8 nm serves as a multi-dentate bridging ligand to coordinate adjacent tetradecanuclear hetero-metal clusters into a 3D pcu-type MOF, where a new topology is observed with the Schläfli symbol of  $(4^{18} \cdot 8^{108} \cdot 12^{27}) \cdot (4)_9$ . In addition, sodium templated effect and photoluminescence property of **1** have been studied.

To the best of our knowledge, the tetradecanuclear  $\{\text{Zn}_{12}\text{Na}_2\}$  hetero-metal cluster is still unexplored and ligand BTDA is firstly involved in the study of metal complex. We believe this work can provide an informative example in preparing functional multi-dimensional hybrid complexes based upon the alkali/transition metal ions and the carboxylate ligands. Thus, further investigations on other type of alkali metal ions and polynuclear transition-metal complexes are being underway.

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#### Appendix A. Supplementary material

CCDC number 923377 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2013.03.009>.

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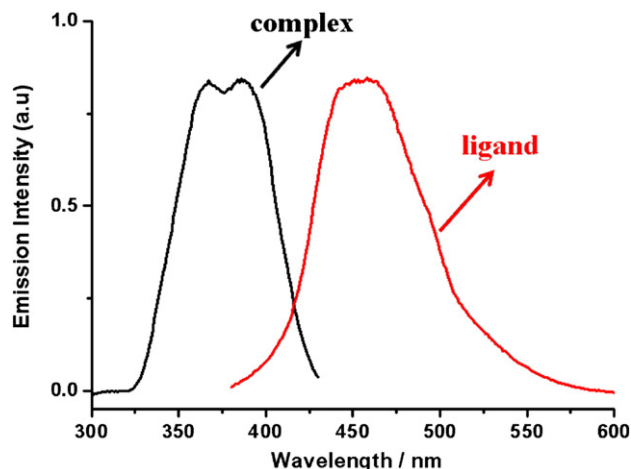


Fig. 3. Solid-state fluorescence emission spectra of H<sub>2</sub>BTDA and complex **1** at room temperature.

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- [17] **Synthesis of 1:** A mixture of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.14 mmol, 52.1 mg),  $\text{H}_2\text{BTDA}$  (0.14 mmol, 72.9 mg),  $\text{NaOH}$  (0.28 mmol, 11.2 mg) and ethanol (10 mL) was sealed into a 20 mL polytetrafluoroethylene-lined stainless steel container, heated at 120 °C under autogenous pressure for 3 days and then gradually cooled to room temperature at a rate of 10 °C · h<sup>-1</sup>. Light yellow prismatic crystals of **1** were isolated in a yield of 38% based on  $\text{H}_2\text{BTDA}$ . Anal. calcd for  $\text{C}_{252}\text{H}_{240}\text{N}_{18}\text{Na}_2\text{O}_{43}\text{S}_{18}\text{Zn}_{12}$  (**1**): C, 53.89; H, 4.31; N, 4.49%. Found: C, 53.63; H, 4.49; N, 4.27%. FT-IR (KBr, cm<sup>-1</sup>): 3436 (b), 2949 (m), 2916 (m), 2863 (m), 1717 (vs), 1652 (m), 1606 (s), 1494 (w), 1427 (m), 1276 (s), 1184 (m), 1105 (vs), 1007 (m), 776 (m), 703(m), 625(m).
- [18] **Structure determination:** A yellow single crystal with dimensions of 0.10 mm × 0.09 mm × 0.09 mm was mounted on a glass fiber for data collection by a Bruker SMART 1 K CCD diffractometer equipped with a graphite-monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Complex **1** crystallizes in a trigonal centrosymmetric space group of  $R\bar{3}$  with  $a = b = 41.4558(13)$ ,  $c = 12.9944(8) \text{ \AA}$ ,  $\alpha = \beta = 90$ ,  $\gamma = 120^\circ$ ,  $V = 19340.0(15) \text{ \AA}^3$ ,  $Z = 3$ ,  $Mr = 5616.12$ ,  $D_c = 1.447 \text{ g/cm}^3$ ,  $\mu = 1.317 \text{ mm}^{-1}$ ,  $F(000) = 8676$ ,  $S = 0.90$  and  $T = 291(2) \text{ K}$ . The final  $R_1 = 0.0745$  and  $wR_2 = 0.2031$  for 3551 observed reflections with  $I > 2\sigma(I)$ . A total of 32902 reflections were collected, of which 7547 were independent ( $R_{\text{int}} = 0.0929$ ). The intensity data set was collected with the  $\omega$  scan mode at 291(2) K in the range of  $1.67 < \theta < 25.00^\circ$  and reduced by SAINT software. The structure was solved by the direct method and refined by full-matrix least-squares techniques on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were added according to the theoretical models. All of the calculations were performed with Siemens SHELXTL™ version 5 package of crystallographic software. The final refinement gave  $(\Delta\rho)_{\text{max}} = 1.21$  and  $(\Delta\rho)_{\text{min}} = -1.84 \text{ e/\AA}^3$ .
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