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Topological Study of Pseudo-Cubic Hydrogen-Bond Networks in a Binary System Composed of Primary Ammonium Carboxylates: An Analogue of an Ice Cube

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Abstract: Hierarchical classification and single-crystal X-ray analysis of unique pseudo-cubic hydrogen-bond networks composed of primary ammonium carboxylates were carried out. The networks consist of four carboxylate anions and four primary ammonium cations at the corners of the cube, and twelve charge-assisted N−H···O hydrogen bonds on the sides of the cube. The configuration of the carboxylate anions generates topological diversity in the network. The results of this hierarchical classification showed that pseudo-cubic hydrogen-bond networks composed of primary ammonium carboxylates can form nine topologically different networks. These pseudo-cubic networks are a subset of the networks formed by octameric water in the form of an "ice cube". The classification system can be applied to other pseudo-cubic networks in a similar way. A survey of crystal structures based on combinations of triphenylacetic acid with various alkylamines (carbon numbers up to eight) and examination of the CSD (Cambridge Structural Database) showed eight salts that form such networks in their crystal structures. These structures are classified into six topologically different networks. Similar networks composed of other salts are also discussed from a topological point of view.

Keywords: ammonium · carboxylates · hydrogen bonds · solid-state structures · topology

Introduction

Topological investigations have been carried out for a wide variety of covalent-bonding networks, such as catenanes and knots,[1] polymers,[2] zeolites,[3] and coordination networks.[4] Hydrogen-bond networks have also been much discussed, because these networks play an important role in the formation of supramolecular assemblies.[5–10] However, the possible topologies of infinite networks are virtually unlimited in number. So far, discussions have mostly been focused on a limited number of small molecules (water,[5,6] alcohols,[7] and some others[8]) and have been based on computer simulations. The fact that these networks are finite enables researchers to search for and discuss all possibilities. One well-known and topologically interesting target is cubic octameric water,[6] known as an "ice cube": a cubic hydrogen-bonded assembly of water molecules which contains twelve O−H···O hydrogen bonds and shows considerable topological diversity (Figure 1a). Here, oxygen atoms occupy the corners of the cube, and the differences in the relative positions of the hydrogen atoms determine the topology. Investigations based on simulations and the graph theory have shown that the ice cube forms 24 topologically different hydrogen-bond networks.[11] Among these, networks with D_{2d} and S_4 symmetry were experimentally detected in the vapour phase by infrared spectroscopy,[12] and networks with C_i and other symmetries[13] were found in the crystalline state. Recently, similar hydrogen-bond networks have been reported for certain organic salts,[14,15] but their topology remains a challenging problem.

Here, we report the topology of pseudo-cubic hydrogen-bond networks composed of primary ammonium carboxylates (Figure 1b). The networks are constructed from four primary ammonium cations and four carboxylate anions with twelve N−H··· hydrogen bonds. We classified these into

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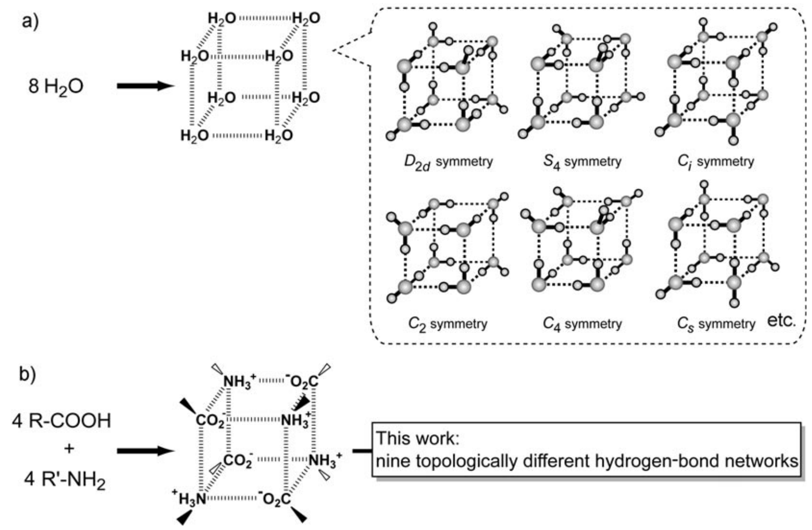


Figure 1. Schematic representations of a) ice cubes with D_{2d}, S_4, C_i, C_2, C_4, and C_s symmetries, b) a pseudo-cubic hydrogen-bond network composed of primary ammonium carboxylate.

nine topologically different networks, and confirmed six of them by single-crystal X-ray analysis. The topology of the networks was found to vary based on slight differences in the substituents of the ammonium cations.

Results and Discussion

Hydrogen-bonding topology of pseudo-cubic networks: "How many hydrogen-bonding topologies can be formed by primary ammonium carboxylates?" To answer this question, we adopted a hierarchical interpretation, which is a very useful tool for interpreting various, often complicated, crystal structures such as cholic acid and brucine.[16] In this work, we employed a hierarchy with three stages, analysing the structure based on the configuration of one carboxylate anion, an ion-pair dimer and an ion-pair tetramer.

In the first stage, we considered the configuration of the carboxylate anion. In the pseudo-cubic network, the carboxylate anion and the ammonium cation act as tridentate hydrogen-bond acceptor and donor, respectively. However, the two oxygen atoms of the carboxylate anion act as different types of acceptor (Figure 2). Therefore, the two oxygen atoms are distinguishable in the pseudo-cubic network: one occupies the corner of the cube and forms two hydrogen bonds (α) and the other occupies the side of the cube and forms one hydrogen bond (β).

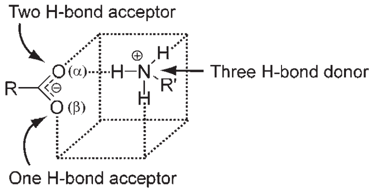
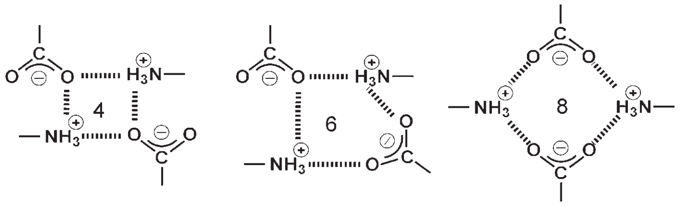


Figure 2. Configuration of carboxylate anion and ammonium cation in the cubic network.

Next, we classified ion-pair dimers incorporating two carboxylate anions. These dimers are easily classified into three different ring types (Scheme 1), denoted as four-, six-, or eight-membered based on the number of heavy atoms participating in the ring. Further classification of the dimer in terms of its position on the face of the cube was carried out (Figure 3a). In the four-membered ring, the two oxygen atoms that participate in the ring each act as an acceptor for two hydrogen bonds, and the other two oxygen atoms occupy the corners of the cube. Since the face containing the four-membered ring has mirror symmetry, it is termed 4m. In the six-membered ring, one carboxylate participates in the ring, so that two different faces are possible. These two faces form an enantiomeric pair, as they are fixed on the surface of the cube and cannot be reversed. Defining the direction of the carboxylate in terms of O(α)-C-O(β), the faces are termed 6c and 6a based on directionality (c: clockwise, a: anticlockwise) of the one carboxylate included in the ring. The eight-membered ring contains two carboxylates with directionality. If both carboxylates are of clockwise or anticlockwise directionality, the face is termed 8c or 8a, respectively; if the two directionalities are opposite, the face contains mirror symmetry and is termed 8m. At this stage, chiral and achiral faces may be distinguished. Among the six faces described above, 4m and 8m are achiral due to the presence of mirror symmetry, while 6c/6a and 8c/8a are chiral faces, and constitute mirror-image isomers of each other. In this way, differences in the two oxygen atoms of the carboxylate anion lead to six faces, including chiral faces.



Scheme 1. Three possible three ring structures for the primary ammonium carboxylate dimer.

In the last stage of cube formation, two faces stack together, and pseudo-cubic networks are formed as tetramers of the ion pair (Figure 3b). In this stage, we consider two modes of stacking: pseudo-cubes AB and ∀B (turned AB). For 4m, 8c, and 8a, the two pseudo-cubes AB and turned

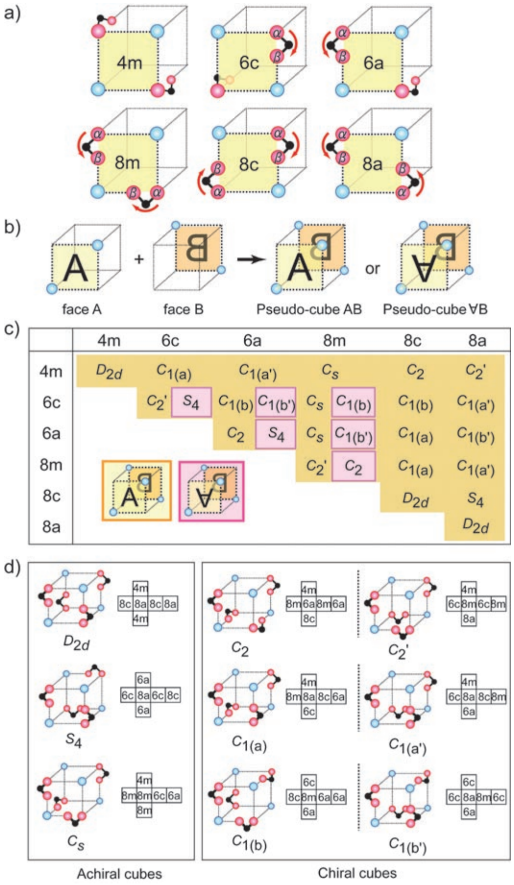
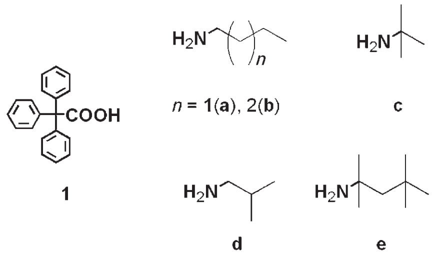


Figure 3. a) Configurations of dimers on the face of the cube. b) Schematic image of pseudo-cube formation through face packing. c) Table for all combinations of two faces. d) Pseudo-cubic hydrogen-bond networks depicted by using opened cubanes and Schoenflies notation (hydrogen atoms are omitted for clarity). Carbon, nitrogen, and oxygen atoms are black, blue, and red, respectively.



Scheme 2. Triphenylacetic acid (**1**), and aliphatic primary amines (**a**–**e**).

AB result in an identical network due to the C_2 symmetry of these faces. In contrast, for the non-C_2-symmetrical faces 6c, 6a, and 8m, the aspects of erected (A) and inverted (∀) toward face B are different. Therefore, we must consider cube ∀B when faces A and B are selected. Since each pseudo-cube is based on three combinations of the two faces, all possible combinations of the six faces may be calculated using the following formula: $({}_6H_2 + {}_3H_2)/3 = 9$.

We examined all of the possible combinations (Figure 3c), and obtained nine pseudo-cubic networks with different topologies: $C_{1(a)}$, $C_{1(a')}$, $C_{1(b)}$, $C_{1(b')}$, C_2, $C_{2'}$, C_s, S_4, and D_{2d} (Figure 3d). Topologies C_2 and C_1 are chiral, with C_2 and $C_{2'}$, $C_{1(a)}$ and $C_{1(a')}$, $C_{1(b)}$ and $C_{1(b')}$ as mirror image isomers of each other, while C_s, S_4 and D_{2d} are achiral; their mirror images are identical to themselves.

Screening of pseudo-cubic networks: We previously reported that *tert*-butylammonium triphenylacetate **1c** (Scheme 2) formed a pseudo-cubic hydrogen-bond network in the crystalline state.[14d] We searched the CSD and found three more primary ammonium carboxylate structures which form pseudo-cubic hydrogen-bond networks (RUTYUA,[14a] LAFDEC[14b] and UMAKOI[14c]). For investigation of further pseudo-cubic networks, we screened salts composed of triphenylacetic acid and alkylamines with carbon numbers up to eight. All of the salts were recrystallized from a mixture of toluene/hexane or benzene/hexane. Single-crystal X-ray analysis revealed that four more salts (Scheme 2, **1a**, **1b**, **1d** and **1e**), in addition to the *tert*-butylammonium salt, formed a pseudo-cubic hydrogen-bond network. Amines smaller than *n*-butylamine were also crystallized, but these formed one-dimensional networks rather than pseudo-cubic networks.

Topologies of pseudo-cubic networks in the crystalline state: A crystallographic study revealed that these five salts form pseudo-cubic hydrogen-bond networks (Figure 4). As the

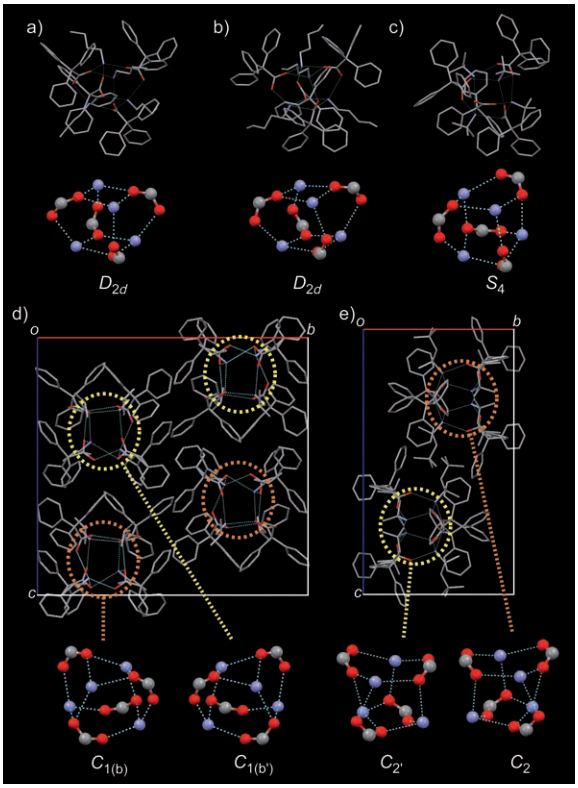


Figure 4. Crystal structures and hydrogen-bond networks of a) **1a** (4:4), b) **1b** (4:4), c) **1c** (4:4), d) **1d** (4:4), and e) **1e** (4:4). Hydrogen atoms are omitted for clarity.

core hydrogen-bond network is surrounded by sterically hindered triphenyl groups and alkyl chains, the pseudo-cubic structures can be said to be reverse micelles. The crystal systems of the structures are tetragonal or monoclinic, not cubic (Table 1). The pseudo-cubic networks consist of twelve N−H··· charge-assisted hydrogen bonds; however, these hydrogen-bond networks are topologically different. Compounds **1a** and **1b** form networks of the same topology, D_{2d}, while **1c** forms an S_4 network. In the case of **1d** and **1e**, two different topologies, which are enantiomers of each other, exist in one crystal as a racemic mixture. In total, there are eight crystal structures with pseudo-cubic hydrogen-bond networks. The distribution of the salts and hydrogen bonding topology are summarized in the Table 2. D_{2d} and S_4 systems have been reported previously, but C_2, $C_{2'}$, $C_{1(b)}$ and $C_{1(b')}$ are new.

Comparison with the ice cube structure: A summary of hydrogen-bonding topologies is shown in Table 3. The results agree with the known topologies of ice cube, except for the fact that two of the ice cube topologies, C_i and C_4, do not exist for primary ammonium carboxylate salts (Figure 5). This is due to the alternating arrangement of the carboxylate anions and ammonium cations that never allows symmetric operations of this type.

Table 2. Topology of pseudo-cubic hydrogen bond networks.

	Compound/Refcode
D_{2d}	**1a**, **1b**, RUTYUA, LAFDEC
S_4	**1c** (IRUOUH), UMAKOI
$C_{1(b)}+C_{1(b')}$	**1d**
$C_2+C_{2'}$	**1e**

Table 3. Comparison of obtained topologies with those of ice cube.

	possible topology
primary ammonium carboxylate	C_1, C_2, C_s, S_4, D_{2d}
ice cube	C_1, C_2, C_4, C_i, C_s, S_4, D_{2d}

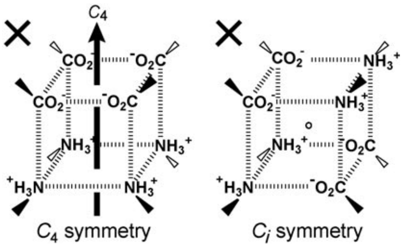


Figure 5. Hypothetical networks with C_4 or C_i symmetry.

The results of energy calculations for ice cube show that the S_4 and D_{2d} topologies are the most stable.[5e] Although it has been suggested that the cubic networks of salts with S_4 and D_{2d} symmetries are more stable than those with other topologies, species with C_1 and C_2 symmetries may be obtained simply by modifying the substituents of the ammonium cations. We suggest that the advantage of packing energy of the external substituents attached to the ammonium ions seems to compensate for the energetic disadvantage of having a network with low symmetry. Therefore, breaking the symmetry leads to the formation of networks with C_1 or C_2 symmetry. We were surprised to find that in the case of RUTYUA and LAFDEC, although the components are chiral, the networks are achiral, with D_{2d} symmetry.[17] These results imply that supramolecular chirality in cubic hydrogen-bond networks does not originate from the chirality of

Table 1. Crystallographic parameters of primary ammonium triphenylacetates.

	1a (*n*-butylammonium)	**1b** (*n*-amylammonium)	**1c**[a] (*tert*-butylammonium)	**1d** (isobutylammonium)	**1e** (*tert*-octylammonium)
formula	$C_{24}H_{27}O_2N$	$C_{25}H_{29}O_2N$	$C_{24}H_{27}O_2N{\cdot}C_3H_3$	$4(C_{24}H_{27}O_2N)$	$2(C_{28}H_{35}O_2N)$
M_r	361.48	375.51	400.53	1445.93	835.18
crystal system	tetragonal	tetragonal	tetragonal	monoclinic	monoclinic
space group	$P\bar{4}2_1c$ (#114)	$I\bar{4}$ (#82)	$I\bar{4}$ (#82)	$P2_1/n$ (#14)	$C2/c$ (#15)
Z	8	8	8	4	8
a [Å]	18.692(1)	18.8561(4)	17.623	13.9624(4)	27.7699(5)
b [Å]	18.692(1)	18.8561(4)	17.623	24.9353(7)	14.0077(3)
c [Å]	11.9668(9)	12.2388(3)	15.181	23.7426(7)	27.6695(5)
α [°]	90	90	90	90	90
β [°]	90	90	90	92.140(2)	111.9577(8)
γ [°]	90	90	90	90	90
V [Å3]	4180.0(5)	4351.5(2)	4714.4	8269.4(4)	9982.5(3)
T [K]	213	213	213	213	213
ρ_{calcd} [Mg m^{-3}]	1.148	1.146	1.129	1.163	1.111
$2\theta_{max}$	136.5	136.3	–	136.4	136.4
$\mu(Cu_{K\alpha})$ [cm^{-1}]	5.66	5.61	–	5.73	5.33
GOF	0.55	2.31	–	1.89	2.28
total/unique reflections	39220/2126	17307/2094	–	57903/14728	45831/9025
reflections used	1371	1838	–	5121	3793
residual electron density max/min [e Å^{-3}]	0.24/−0.18	0.19/−0.26	–	0.70/−0.56	0.75/−0.82
reflections/parameters	8.71	8.28	–	9.00	9.31
$R1$[b]/$wR2$[c]	0.037/0.102	0.069/0.178	–	0.148/0.294	0.113/0.250

[a] Data from refererence [14d] (IRUOUH). [b] $I > 2.00\delta(I)$. [c] All data.

the molecules contained therein. Similar results are often seen for dimer hydrogen bonds,[18] and our results imply that these are applicable to tetramers.

Topological studies of other pseudo-cubic networks: We also focused on the topologies of similar networks containing different components. To date, the following organic salts have been reported: primary ammonium with chloride (Figure 6a),[15a] thiolate (Figure 6b),[15b] sulfonate (Figure 6c),[15c] and phosphonothioate (Figure 6d).[15d] In the first two salts, each anion accepts three hydrogen bonds at a single atom such as chlorine or sulfur. Therefore, these networks show nearly tetrahedral symmetry. In the sulfonate anion, the three oxygen atoms each accept one hydrogen bond. Since these three atoms are not distinct, only one network is possible. The last example, the phosphonothioate anion, is analogous to the carboxylate anion; the oxygen and sulfur atoms are equivalent to O(α) and O(β), respectively, on the assumption that the oxygen atom of the phosphonothioate forms two hydrogen bonds, while the sulfur atom forms one. This tells us that this salt is capable of forming nine topologically different hydrogen-bond networks. These comparisons suggest that for ammonium salts, the anion holds the balance of topological diversity.

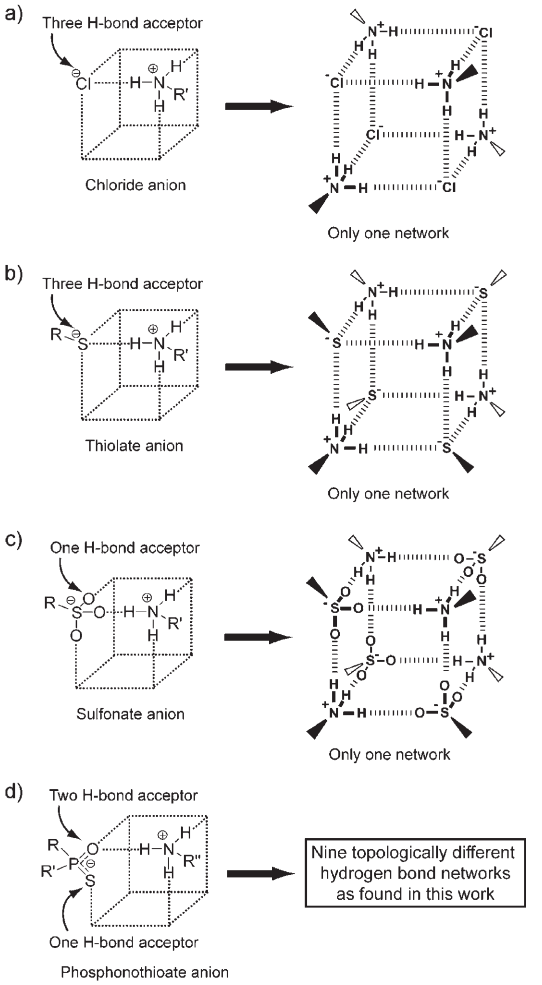


Figure 6. Pseudo-cubic hydrogen bond networks composed of primary ammonium a) chloride, b) thiolate, c) sulfonate, and d) phosphonothioate.

Conclusion

We demonstrated that pseudo-cubic hydrogen-bond networks composed of primary ammonium carboxylates may be classified into nine networks with different topologies. Application of this hierarchical interpretation, beginning with the configuration of the carboxylate anion, results in the identification of six different faces (by distinguishing the two oxygen atoms), and, in the end, nine different cubic hydrogen-bond networks (based on stacking of two faces to form a cube). The results imply homology between the networks of primary ammonium carboxylates and those of an ice cube. Furthermore, the theory was confirmed based on the X-ray crystal structures of these species.

In conclusion, we carried out a theoretical classification of the topological differences among pseudo-cubic hydrogen-bond networks, and examined actual pseudo-cubic networks by employing triphenylacetate salts. These differences in topology contribute towards a structural understanding that will be useful for such applications as optical resolution and metal-free absolute asymmetric synthesis. The hierarchical classification system used in this work will form the basis of a widely useful approach for analysis of more complicated supramolecular assemblies.

Experimental Section

Materials: Reagents were purchased from Tokyo Chemical Industry. Single crystals were prepared by recrystallization from a mixture of toluene/hexane or benzene/hexane.

Data collection: X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). Lattice parameters were obtained by least-squares analysis from reflections for three oscillation images. Structure solution was achieved by direct methods, SIR92. The structures were refined by a full-matrix least-squares procedure with all the observed reflections based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions with isotropic displacement parameters relative to the connected non-hydrogen atoms, and not refined. All calculations were performed using the TEXSAN[19] crystallographic software package.

CCDC-615498 (**1a**), CCDC-632004 (**1b**), CCDC-632005 (**1d**), CCDC-632006 (**1e**) contain 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.

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