Fourfold Diamond Structure of the Dipotassium and Disodium Salts of 1,3,5,7-Adamantanetetracarboxylic Acid

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The (isomorphous) crystal structures of the dipotassium and disodium salts of 1,3,5,7-adamantanetetracarboxylic acid are described. In the tetragonal, non-polar crystals of space group $P4_2/nbc$ the tetrahedral dihydrogen tetracarboxylate anions join to form four hydrogen-bonded superdiamond networks interpenetrating each other. The cations are arranged in chains ("metal-over-metal") within fourfold helical channels (double antiparallel double-helices). The short, negatively charged $O-H \cdots O^\ominus$ hydrogen bonds are symmetric on average. However, in the dipotassium salt actually disordered, asymmetric hydrogen bonds are likely to be present (double-minimum potential, $O-H \cdots O^\ominus$ distance 2.52 Å). In analogy to potassium dihydrogen phosphate, KH_2PO_4, the present tetra-hedral dipotassium dihydrogen tetracarboxylate may thus potentially form polar, ferroelectric crystals at low temperature with an ordered array of asymmetric hydrogen bonds. In the course of the crystallization of the disodium salt of adaman-tanetetracarboxylic acid, tetragonal crystals of a tetrahydrate of the tetrasodium salt were accidentally obtained (space group $I4_1/a$) and their structure determined. The arrangement of the hydrated anions may be characterized either as a hy-drogen-bonded, distorted triple-diamond structure, or else as a "semi-clathrate", consisting of non-intersecting orthogonal water chains interpenetrating each other and tetracarboxylate tetraanions functioning as cross-links between these chains by means of hydrogen bonds.

Introduction

The molecules of 1,3,5,7-adamantanetetracarboxylic acid (1) have tetrahedrally directed carboxylic groups and join to form five large and hollow superdiamond networks in the crystal, which interpenetrate in order to avoid open cavities[1]. Similarly, the smaller molecules of methanetetra-acetic acid $C(CH_2CO_2H)_4$ (4) build up a distorted triple-diamond structure in the crystal[2]. A comparable, largely undistorted triple-diamond structure forms the host lattice of a solid-state inclusion compound 5 · HOAc of 2,6-dioxo-1,3,5,7-adamantanetetracarboxylic acid hydrate (5) with acetic acid as molecular guest[3]. Within the individual dia-mondoid networks the tetracarboxylic acid molecules are held together by the usuall pairwise hydrogen bonds

1: M = H
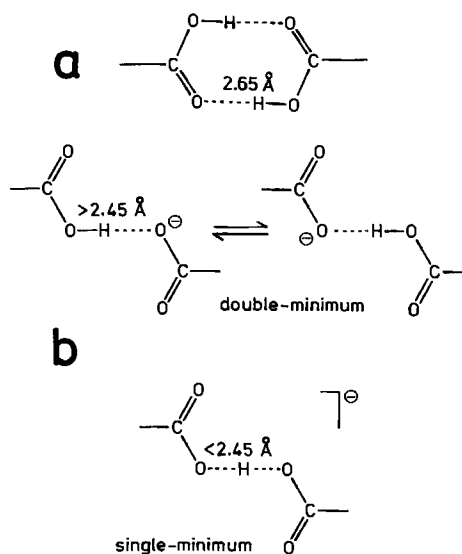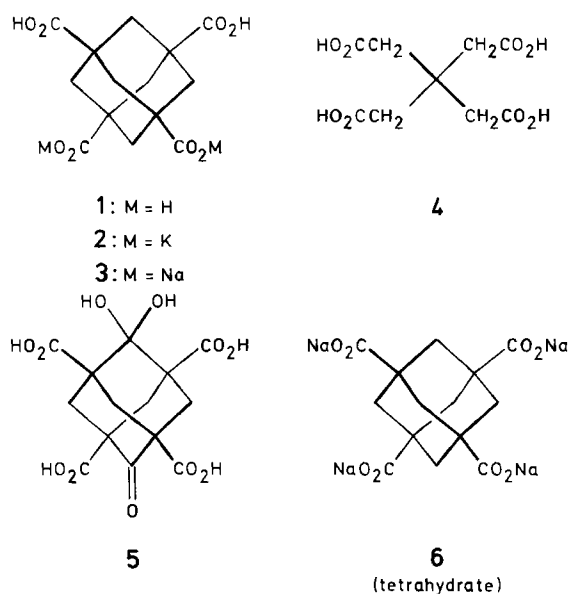2: M = K
3: M = Na

4

5

6
(tetrahydrate)

Figure 1. (a) Usual pairwise hydrogen bonding between approxi-mately colinear and coplanar carboxylic groups. (b) Asymmetric and symmetric alternatives of negatively charged hydrogen bonds in half-deprotonated carboxylic acids. The singly hydrogen-bonded, coplanar carboxyl(ate) groups are laterally displaced. Estimated preferred O(H)O distances and rough distance limits, respectively, are given

as shown in Figure 1a. The disposition of the carboxylic groups is colinear to a good degree of approximation, and the preferred O(H)O distance amounts to about 2.60 to 2.65 Å.

A novel variant of multiple superdiamond structures based on tetrahedral tetracarboxylic acids may be formally designed by removing one proton from the pairs of hydrogen bonds and hence generating single, charged $OHO^{\ominus}$ bridges. As shown in Figure 1b, intermolecular bridges of this kind have a laterally displaced structure, i.e. the carboxylic groups are no longer facing each other colinearly. Due to the negative charge, these hydrogen bonds are particularly strong and short, such that ultimately a symmetric structure may evolve whose proton dynamics is to be described by a single-minimum potential. As a rule of thumb it may be stated that an O(H)O distance less than 2.45 Å may give rise to a symmetric $O \cdots H \cdots O^{\ominus}$ hydrogen bond (single-minimum potential), whereas otherwise usually unsymmetric $O-H \cdots O^{\ominus}$ bridges (double-minimum potential) are indicated[4].

This concept thus leads to tetrahedral dihydrogen tetracarboxylates, and we describe here as first and prototypal cases the crystal structures of the dipotassium salt 2 and disodium salt 3 of 1,3,5,7-adamantanetetracarboxylic acid. The structure analyses chiefly served to answer the following questions: Are interpenetrating diamondoid, anionic networks indeed formed? If so, what is the degree and mode of interpenetration? What is the shape of the cavities housing the cations? How long are the hydrogen bonds, i.e. are they symmetric or unsymmetric? Answering these questions is also of interest in relation to the structure of potassium dihydrogen phosphate KH_2PO_4, whose anions form a distorted diamondoid network in the crystal, held together by single $O-H \cdots O^{\ominus}$ hydrogen bonds very much as discussed here for tetrahedral dihydrogen tetracarboxylates. The question in this respect is, above all, whether this analogy may possibly be extended to electrical properties. This could be of some importance considering the ferroelectricity of KH_2PO_4 at temperatures below 123 K[2]. The present paper reports on the structural properties of the two tetrahedral dihydrogen tetracarboxylates 2 and 3, and also of the tetrasodium salt (tetrahydrate) 6 of 1, which was obtained accidentally in the course of the crystallizations. Investigations relating to possible phase transitions, polar crystal forms and electrical properties are planned and deferred to a later publication.

Results and Discussion

The crystal structures of the dipotassium salt 2 and the disodium salt 3 of adamantanetetracarboxylic acid 1 are isomorphous (see Experimental). Therefore, they differ only gradually, yet significantly and characteristically depending upon the different cationic radii ($K^{\oplus}$ 1.33, $Na^{\oplus}$ 0.95 Å[5]). Since the structure of the dipotassium salt 2 is more interesting and somewhat more precise than that of the disodium salt 3, all figures concerned were based on the results of 2. The refined atomic coordinates of 2 and 3 appear in Tables 1 and 2, respectively. The intramolecular geometries of the dihydrogen adamantanetetracarboxylate anions of 2 and 3 are rather unexceptional, and we do not deal with any details here; a few more relevant data are included in Figure 2. The salts 2 and 3 crystallize in the centrosymmetric (i.e. nonpolar) tetragonal space group $P4_2/nbc$ with four formula units per unit cell. As illustrated by the symmetry diagram of Figure 2, the adamantanetetracarboxylate anions possess S_4 symmetry while the alkali cations occupy sites of D_2 symmetry (ordered) and C_2 symmetry (partially disordered, two alternative positions with half-occupancy). As envisaged, the carboxyl and carboxylate groups, respectively, are connected by short, single O(H)O hydrogen bonds, which are centrosymmetric on average and correspond to the planar displaced type shown in Figure 1b (see also further below).

In the crystals of 2 and 3, the dihydrogen tetracarboxylate anions indeed join to form large and open diamondoid networks held together by the negatively charged hydrogen bonds just described. Thus, the high propensity of formation and strong structural "building power" of hydrogen-bonded

Table 1. Atomic coordinates, weights (g), and anisotropic temperature factor coefficients of 2 (estimated standard deviations in parentheses); positional parameters of K, C, O multiplied by 10^4, all other quantities by 10^3; anisotropic temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^* + \cdots)]$; weights of K positions adjusted with the help of corresponding electron density maxima of a Fourier map; hydrogen parameters assumed; see Figure 2 for atomic numbering (H_{ox}: carboxyl hydrogen)

	x	y	z	g	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	2500	2500	2500	190	97(3)	$=U_{11}$	118(5)	0	0	48(4)
K(2)	2500	1480(10)	0	280	66(4)	148(8)	126(6)	0	-43(4)	0
K(3)	2500	0	0	30	135(21)					
C(1)	8106(6)	1440(6)	3143(4)	1000	46(3)	36(3)	21(2)	-1(2)	-2(2)	8(3)
C(2)	7064(6)	840(6)	2500(5)	1000	56(4)	32(3)	29(2)	2(3)	6(3)	-4(2)
C(3)	7500	2500	3762(4)	500	56(5)	38(4)	17(3)	0	0	14(4)
C(4)	8740(9)	403(7)	3808(5)	1000	74(4)	44(4)	36(3)	-7(3)	6(4)	19(3)
O(1)	9583(6)	815(6)	4398(4)	1000	79(4)	69(4)	58(3)	7(3)	-32(3)	20(3)
O(2)	8421(8)	-733(5)	3744(5)	1000	145(7)	48(4)	81(4)	9(3)	-30(4)	14(3)
H(2A)	639	41	290	1000	68					
H(2B)	746	15	209	1000	68					
H(3)	818	289	419	1000	68					
H_{ox}	987	26	481	500	100					

Table 2. Atomic parameters of 3. Caption of Table 1 carries over

	x	y	z	g	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	2500	2500	2500	220	96(7)	$=U_{11}$	57(7)	0	0	1(10)
Na(2)	2500	1450(18)	0	250	80(12)	67(12)	85(12)	0	-53(12)	0
Na(3)	2500	2500	0	30	101(37)					
C(1)	8110(10)	1382(11)	3132(6)	1000	24(5)	24(6)	18(5)	5(4)	-7(4)	5(4)
C(2)	6980(9)	790(10)	2487(8)	1000	24(5)	20(6)	20(4)	-1(4)	-2(5)	-3(4)
C(3)	7500	2500	3757(7)	500	31(8)	33(8)	12(5)	0	0	18(10)
C(4)	8685(12)	293(13)	3806(9)	1000	39(7)	52(8)	21(5)	8(5)	6(5)	30(6)
O(1)	9624(10)	756(10)	4380(5)	1000	66(7)	71(7)	29(4)	12(5)	-15(5)	31(5)
O(2)	8262(11)	-898(9)	3778(7)	1000	74(7)	36(5)	57(6)	24(5)	-1(5)	14(4)
H(2A)	625	37	290	1000	43					
H(2B)	735	4	209	1000	43					
H(3)	821	289	419	1000	43					
H$_{ox}$	1000	0	500	500	6(28)					

superdiamond architectures are once again manifest. It should also be noted in this context that 2 and 3, although crystallized from aqueous solutions, do not form hydrates. A space-filling representation of a superadamantane section is shown in Figure 3 in order to realistically illustrate the hollowness of the superdiamond frameworks. These cavities are chiefly filled by three interpenetrating, equivalent frameworks such that altogether four diamondoid networks are interwoven (concatenated). Obviously, smaller cavities still have to be kept open in order to accommodate the cations. On the basis of adamantanetetracarboxylic acid 1 we have now realized a contiguous row of multiple superdiamond structures with the degrees of interpenetration (= number of interpenetrating networks) 5[1], 4, 3[3], and 2[6].

Figure 4 illustrates the mode of interpenetration, i.e. the way the four anionic superdiamond networks of 2 and 3 interpenetrate (adamantane cores shown as spheres, hydrogen-bridged carboxylate groups as interconnecting rods). Opposite centers of a superadamantane section cut out of a superdiamond lattice have a distance of $2c$ along the c axis and of $2a$ along the a and b axes (Figure 2) such that tetragonal elongations (= axial ratio c/a) by factors of 1.351 and 1.424, respectively, result for 2 and 3. The four individual superdiamond networks are shifted with respect to one another by $c/2$, i.e. by one quarter of the "long diagonal" of a superadamantane unit. Although the networks are equidistant and symmetry-equivalent, translational equivalence exists only between every second diamondoid anionic net-

Figure 2. Space group symmetry diagram of 2 (and similarly 3), projected along the tetragonal c axis. The symmetry elements of the space group $P4_2/nbc$ are shown, except for glide planes and 2_1 screw axes (unit cell origin on center of symmetry). Elevations of the molecular centers (S_4 axes) are given in units of c. Ten molecules of 2 are shown (heavy lines) forming an elongated superadamantane framework (Figure 3). Two central molecules are superimposed in this projection. Four additional molecules of an adjacent superdiamond network related by the twofold axis at $1/4,y,-1/2$ are drawn in light lines in order to point out the non-translational equivalence and to illustrate the cross-section of the fourfold helical channels housing the cations. The $K^{\oplus}$ ($Na^{\oplus}$) ions appear as full circles (ordered) and open circles (disordered, half-occupancy; see text), respectively. The single $O(H)O^{\ominus}$ hydrogen bonds are represented as dashed lines, and $O(H)O$ as well as CO distances are included for 2 and (in parentheses) 3. Atomic labels appear in the lower right part of the diagram
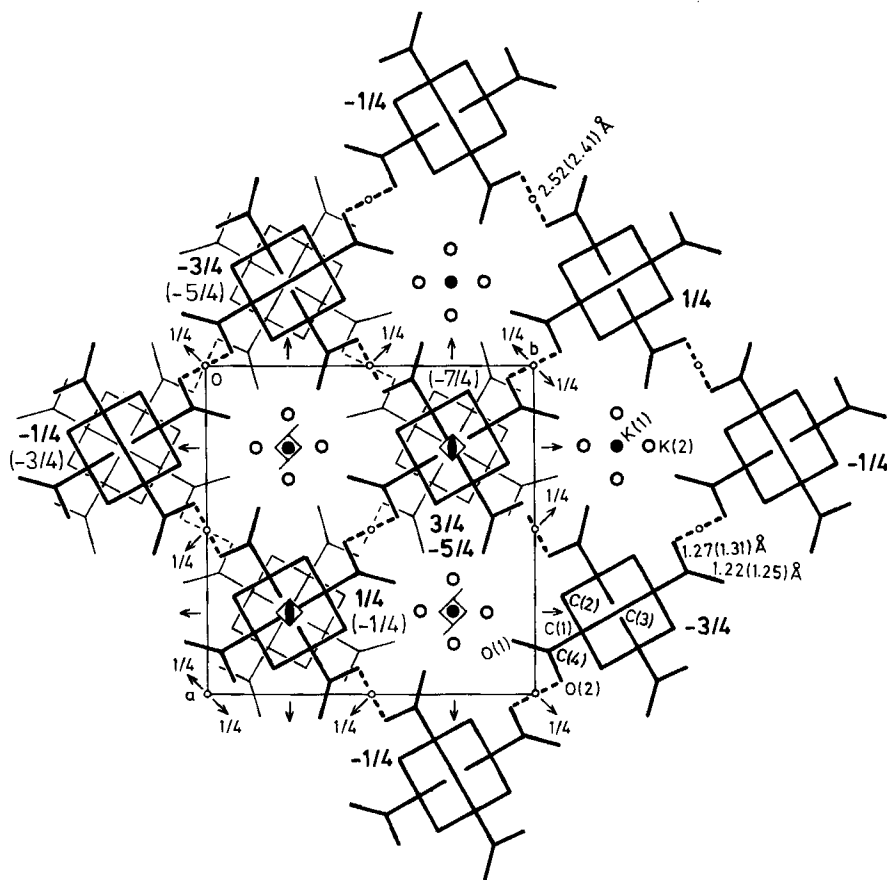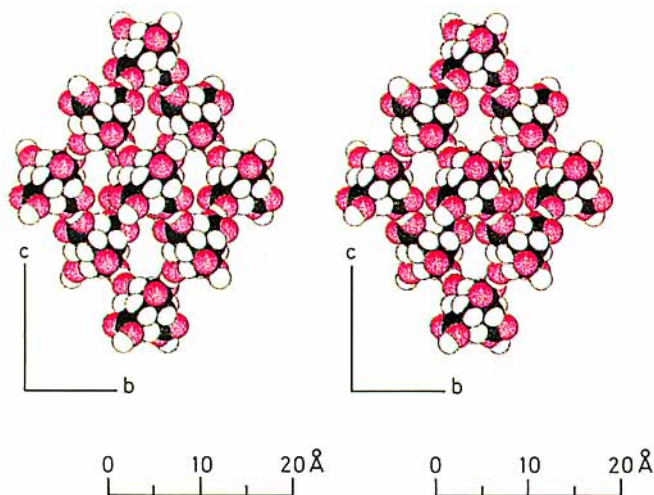
Figure 3. Space-filling stereoview of a hydrogen-bonded, anionic superadamantane unit cut out of a diamondoid network of **2** (and **3**; oxygen atoms in red). The large central cavity is filled in the crystal by three equivalent interpenetrating networks (and the cations)
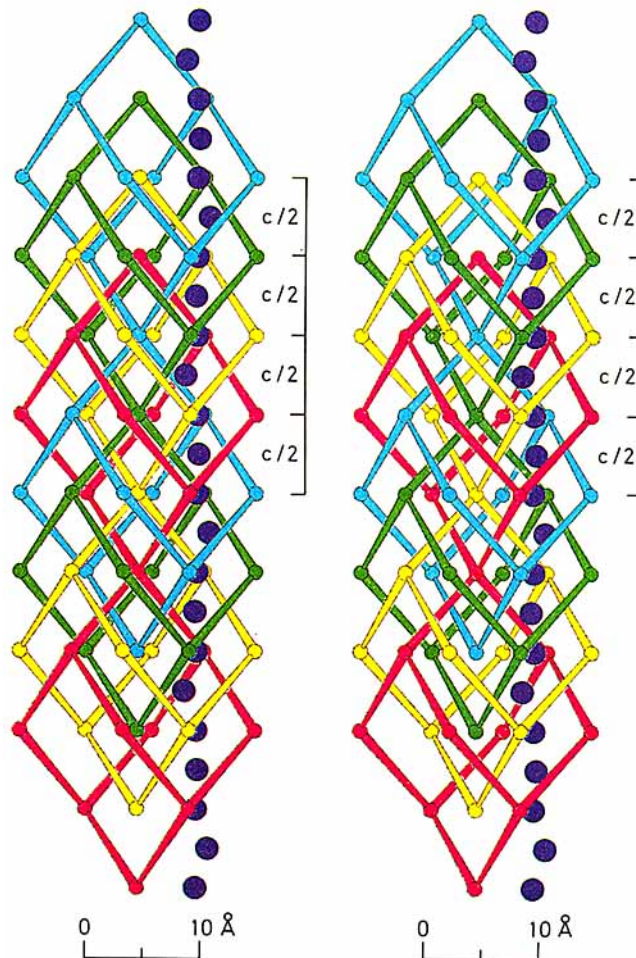

Figure 4. Schematic stereoview of the four interpenetrating diamondoid networks of **2** (and **3**; blue, green, yellow, red) represented by two connected superadamantane units. Note that only next but one networks are translationally equivalent (see text). The small spheres of the networks represent the adamantane cores (on S_4 axes), and the interconnecting rods symbolize the carboxyl(ate) groups joined by negatively charged, single hydrogen bonds. One chain of cations (in violet) within a fourfold helical channel is shown. Due to disorder, the lateral displacement (away from the 4_2 screw axis) of every second cation is partially arbitrary

work. Neighboring networks are related by twofold rotation axes perpendicular to the tetragonal c axis (Figures 2, 5, 6; these different equivalencies are not evident from the simplified Figure 4). On closer inspection, the present fourfold diamond structure thus turns out to be a double double-diamond structure. Along the 4_2 screw axes this fascinating architecture gives rise to the formation of channels, which accommodate the cations.

The mode of interpenetration of **2** and **3** is largely analogous (or rather homologous) to that of the threefold diamond structure occuring in the above-mentioned inclusion compound **5** · HOAc between the dioxoadamantanetetracarboxylic acid hydrate **5** and acetic acid[3]. [This holds similarly for methanetetraacetic acid (**4**) whose triple-diamond structure is of the same mode as in this inclusion compound[2]. Contrary to **2** and **3**, the superdiamond networks of **5** · HOAc and **4** are all translationally equivalent.] The fourfold diamond structure of **2** and **3** may be lucidly developed out of the triple-diamond structure of **5** · HOAc as follows: The superdiamond networks of **5** · HOAc are practically undistorted, and the distance between opposite adamantane centers amounts to about 23 Å. This distance corresponds approximately to three times the thickness of an adamantane core (ca. 7.3 Å), such that the threefold interpenetration in **5** · HOAc may readily be accomplished in the mode discussed here. However, relatively wide channels remain open in this architecture, which are filled by the acetic acid guest molecules. A similar, homologous fourfold interpenetration may therefore only be attained by a substantial tetragonal elongation, which in the case of uncharged pairwise hydrogen bonds between the carboxyl groups as in **5** · HOAc would lead to considerable strain. In contrast to **5** · HOAc, the single charged hydrogen bridges of **2** and **3** do no longer involve colinear carboxyl(ate) groups (Figures 2, 3, 5), and the elongation of the superdiamond networks (Figures 3, 4) required for the fourfold

interpenetration may be realized practically strain-free through appropriate rotations of the carboxyl(ate) groups about the $C(sp^3) - C(sp^2)$ bonds. Necessarily, this elongation is accompanied by a narrowing of the open channels, which turns out to be just of the right proportion for fitting in the relatively small (compared to acetic acid) potassium and sodium cations. The difference between the elongation factors of **2** and **3** mentioned above is as expected, since the larger potassium ions require wider channels leading to a smaller elongation (accompanied by a lengthening of the hydrogen bonds; see below). Like the acetic acid complex of **5**, the salts **2** and **3** thus possess characteristics of channel inclusion compounds.

The potassium and sodium ions of **2** and **3** are arranged in chains ("metal-over-metal") along the 4_2 screw axes (channel axes) with a moderate statistical lateral displacement (ca. 1.0 Å) of every second ion along the a or b axis (Figures 2, 4, 5; $K^\oplus \cdots K^\oplus$ and $Na^\oplus \cdots Na^\oplus$ distances 3.629 and
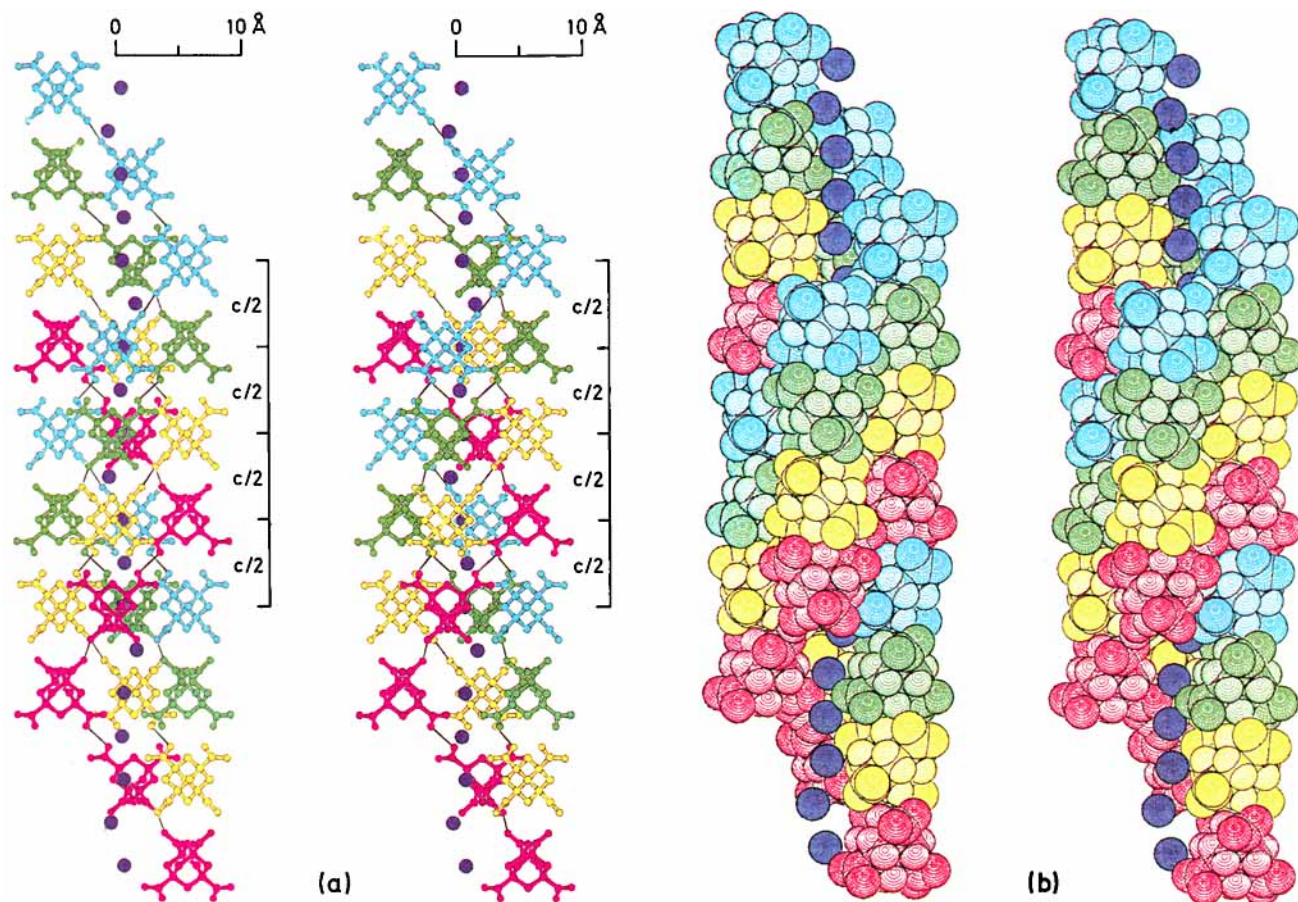
Figure 5. Stereoview of the fourfold helical architecture of the channels accommodating the cations in **2** (and **3**). The illustrations show clearly that adjacent helices are not translationally equivalent. The lateral displacements of the cations (in violet) from the 4_2 chain axis are partially arbitrary. (a) Ball-and-stick representation with all hydrogen atoms omitted. The single, charged hydrogen bonds are indicated by thin black lines. (b) Space-filling representation of same scale as (a)

3.656 Å, respectively; see Experimental). Thus, within multiple superdiamond structures of tetrahedral dihydrogen tetracarboxylates columnar arrangements of metal ions may be realized, and it is tempting to speculate about interesting conductivity properties if structurally similar salts with heavy-metal cations of suitable redox behavior could be prepared[7].

The structure of the channels housing the cations in **2** and **3** may be viewed as a fourfold helix, since the diamond lattice is describable as a system of heavily cross-linked four-storeyed screws (cf. the analogous triple-helical host channels in the acetic acid inclusion compound of **5**[3]). A section of this beautiful supramolecular architecture is shown in Figure 5. Like the four interwoven superdiamond networks, the four coaxial, singly hydrogen-bonded helices are equidistant, yet not all translationally equivalent. Neighboring helices are related by twofold axes perpendicular to the helical axis (4_2) and are therefore antiparallel. It follows that next but one coaxial helices are translationally equivalent. On closer inspection, the present fourfold helix is therefore revealed to be a double antiparallel double helix (Figures 2, 5). For illustration, the characteristics of this unusual structure are highlighted once again by the idealized representation of Figure 6. Mention should be made here of the well-known

fact that the sugar – phosphate chains of the two famous coaxial (but not equidistant) helices of deoxyribonucleic acid (DNA) also run in opposite directions[8].

The metal ions in the channels of **2** and **3** are coordinated by oxygen atoms protruding into the interior of the helices [fourfold, very severely distorted tetrahedral coordination; $K^{\oplus}(Na^{\oplus}) \cdots O$ distances between 2.522 (2.334) and 2.740 (2.617) Å]. The $K^{\oplus}$ ($Na^{\oplus}$) ions on the D_2 sites are coordinated to four oxygen atoms belonging to different helices, while those on the C_2 sites are coordinated to pairs of oxygen atoms of two neighboring helices. It may be seen from the space-filling picture of Figure 5b that the shape of the channel walls resembles that of a ball condenser with the metal ions located in the spherical cavities.

The $O(H)O^{\ominus}$ hydrogen bonds of **2** and **3** extend across crystallographic centers of symmetry and are therefore symmetric *on average* (Figure 2). This is compatible with ordered, truly symmetric (single-minimum potential) structures as well as disordered, asymmetric (double-minimum potential) arrangements. The present X-ray data do not provide direct evidence in favor of either of the two possibilities, since they do not allow to localize reliably the bridging hydrogens (see Experimental). As expected, the O(H)O distance of the dipotassium salt **2** [2.52(1) Å] is longer than
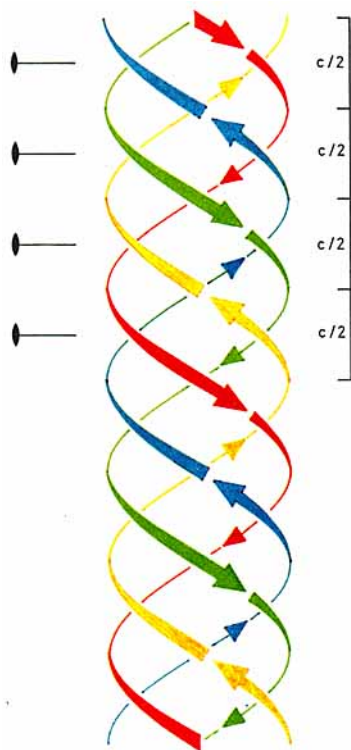
Figure 6. Diagrammatic representation of the double antiparallel double-helix (fourfold helix) present in **2** (and **3**). The directionality of the helices is highlighted by arrows. It may be seen that the twofold axes perpendicular to the common helical axis relate neighboring helices and thus impose opposite directionalities on them. Neighboring helices are therefore antiparallel while next but one helices are parallel. Inspection of Figure 2 shows that there are altogether four sets of perpendicular twofold axes of which only one set is represented here. The common axis of the four helices coincides with a 4_2 screw axis and therefore also with a twofold axis relating parallel helices. Note that the perpendicular twofold axes do not run through the helical chains yet pass half-way between them. The helices are therefore polar and possess directionality

the crystallization experiments of the disodium salt **3** (see Experimental). These tetragonal crystals of space group $I4_1/a$ were also subjected to a detailed X-ray analysis and turned out to consist of a tetrahydrate **6** of the tetrasodium salt. In complete analogy with **4**, which also crystallizes in space group $I4_1/a^{2)}$, the crystal structure of the tetrahydrate **6** may be described as a tetragonally elongated triple-diamond structure with translationally equivalent (along the c axis) superdiamond networks. Tetrahydrated tetracarboxylate anions may be identified as tetrahedral building blocks, which are linked diamond-like by single $O-H \cdots O$ hydrogen bonds between water molecules (across centers of
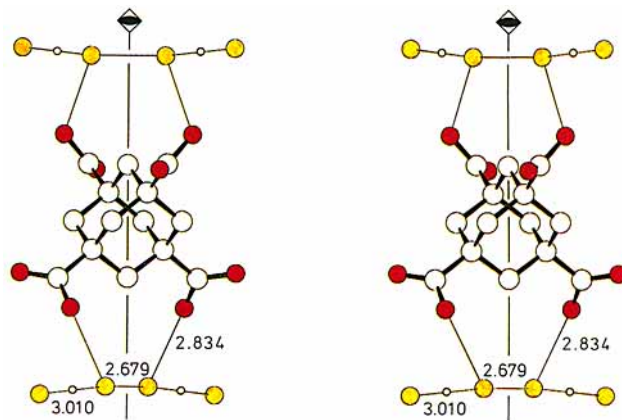

Figure 7. Stereoview of a tetrahedral building block of **6** consisting of a tetrahydrated adamantanetetracarboxylate tetraanion (carboxylate oxygen atoms in red, water oxygen atoms in yellow). Four additional, hydrogen-bonded water oxygen atoms are shown in order to illustrate the water chains. All hydrogen atoms have been omitted. The hydrogen bonds [thin lines, with O(H)O distances in Å] across the twofold axis and the centers of symmetry (small circles) are twofold disordered
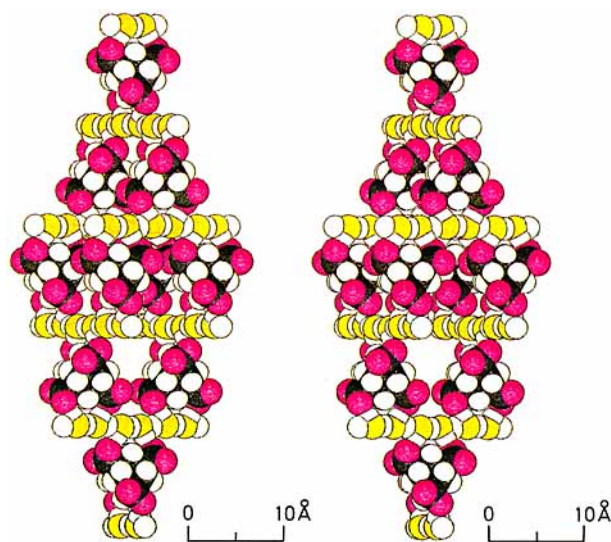
that of the disodium salt **3** [2.41(1) Å], since in this way an increased channel width is generated as required for the accommodation of the larger potassium ions. From the O(H)O distances of **2** and **3**, it may be tentatively concluded that the former involves asymmetric hydrogen bonds with a double-minimum potential ($O-H \cdots O^{\ominus}$), whereas for the latter the symmetric single-minimum alternative ($O \cdots H \cdots O^{\ominus}$) is more likely. With reference to KH_2PO_4 [O(H)O distance, 2.49 Å][9], the conditions for ferroelectricity at lower temperatures would therefore in particular be met by the dipotassium salt **2**, provided a phase transition indeed occurs, which leads to a polar crystal structure combined with an ordering process of the asymmetric $O-H \cdots O^{\ominus}$ hydrogen bonds. Experimental work is planned in order to probe these conjectures. At any rate, the investigations reported here already show that tetrahedral dihydrogen tetracarboxylates in principle possess the crystal-structural potential to bring about interesting ferroelectric behavior.

As noted briefly in the Introduction, crystals of the tetrasodium salt of **1** were accidentally obtained in the course of

Figure 8. Space-filling stereoview of a superadamantane unit of **6** (tetragonal c axis vertical; carboxylate oxygen atoms in red, water oxygen atoms in yellow; for convenience of drawing, the bridging hydrogen atoms in the water chains have been placed symmetrically between the oxygen atoms). The substantial tetragonal elongation is evident. The open spaces of this architecture are filled in the crystal by two interpenetrating, translationally equivalent superdiamond networks and the sodium cations

symmetry). A stereoview including hydrogen-bond lengths is shown in Figure 7. These distorted tetrahedral units possess (average) S_4 symmetry, and their relatively large extension along the c axis gives rise to a correspondingly large tetragonal elongation of the superdiamond frameworks by a factor of $3c/(\sqrt{2}\ a) = 2.657$. A good pictorial impression of this architecture is provided by the space-filling stereodrawing of Figure 8 showing a superadamantane unit cut out of a superdiamond network. The hydrogen bonds across the (average) twofold axes and the (average) centers of symmetry are disordered. The hydrogen-bonded threefold superdiamond structure of **6** still involves small cavities, which are taken up by the $Na^{\oplus}$ ions. The resulting oxygen coordination of the cations is fivefold with $Na-O$ distances between 2.269 and 2.513 Å (four sodium—carboxylate contacts and one sodium—water contact). Finally, it is noted that the cations of **6** are not arranged in chains as in **2** and **3**, but rather in eight-membered rings of S_4 symmetry with alternating sodium ions and (carboxylate) oxygen atoms.

The structure of **6** may also be described as consisting of two sets of non-intersecting, hydrogen-bonded chains of water molecules, which interpenetrate perpendicularly (parallel to the a and b axes, respectively). The $O-H \cdots O$ hydrogen bonds within the almost straight water chains are twofold disordered and may be viewed as "flip-flop" bonds[10]. The tetracarboxylate anions act as cross-links between orthogonal water chains by four ordered $O-H \cdots O^{\ominus}$ hydrogen bonds (Figures 7 and 8). It therefore appears that the structure of **6** represents a clathrate, albeit not a "true clathrate"[11a] but only a "semi-clathrate"[11b], since hydrogen bonds are observed not only within the water host alone, yet also between this host and the anionic tetracarboxylate guest molecules.
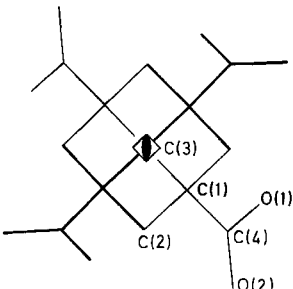
Experimental

The crystallization and structure analysis of the disodium salt **3** was performed first, and the experiences gained were taken advantage of in the subsequent investigation of the dipotassium salt **2**. The interest in **2** was stimulated chiefly by the expected lengthening of the hydrogen bonds as compared to **3**, which is important in regard of interesting ferroelectric properties. The additional hope for a fully ordered arrangement of the potassium ions in **2** proved futile, however.

Disodium Dihydrogen 1,3,5,7-Adamantanetetracarboxylate (**3**): $C_{14}H_{14}O_8Na_2$, $M_r = 356.24$. — Crystallization: **1**[12] was half-neutralized with 0.1 n aqueous NaOH and the water slowly evaporated. After about two weeks three different types of crystals had formed concurrently: a) large tetragonally elongated octahedra (tetragonal bipyramids), which according to their cell dimensions were identified as the free tetracarboxylic acid **1**; b) large, water-clear crystals devoid of a characteristic shape, which a full X-ray analysis revealed to be a tetrahydrate of the tetrasodium salt **6** of the adamantanetetracarboxylic acid **1** (see below); c) spear-shaped crystals of partially dendritic character, which turned out to be the sought disodium salt **3**. — Crystal data and X-ray analysis of **3**: Tetragonal space group $P4_2/nbc$ (No. 133), $Z = 4$, $a = 9.850(2)$,

$c = 14.027(3)$ Å; $\varrho_{calcd.} = 1.739$ gcm^{-3}, $\varrho_{found} = 1.73$ gcm^{-3} (CCl_4/CH_2Br_2, flotation). The intensity measurements were performed at room temp. on a CAD-4 four-circle diffractometer ($\lambda_{Mo} = 0.71069$ Å, $\Theta_{max} = 27°$); structure solution with direct methods; C, O, Na anisotropically refined, H positions constructed and not refined, bridging hydrogen atoms fixed on symmetry centers; totally 340 reflections with $F_o > 4\sigma(F_o)$ included in the refinements; $R = 0.125$, $R_w = 0.134$ [$\Sigma w(\Delta F)^2$ minimized, $w = 1/\sigma^2(F_o)$]; programs used: SDP, SHELX 76[13]; refined atomic parameters in Table 2[14]. The average crystallographic symmetry of the dihydrogen tetracarboxylate anions is S_4. Four $Na^{\oplus}$ ions reside ordered on the D_2 site at 1/4,1/4,1/4, and four others disordered on the C_2 site at 1/4,y,0 (half-weights). The symmetry-related position $1/4,1/2 - y,0$ cannot be occupied simultaneously by a $Na^{\oplus}$ ion, since the distance between both positions is too small (2.07 Å). This results in the above-mentioned $Na^{\oplus}$ chains every second cation of which is laterally displaced (statistically along the a or b axis) by about 1.0 Å with respect to the 4_2 chain axis. A certain small residual electron density was encountered on the D_2 site at 1/4,1/4,0, which was considered as a slightly occupied third $Na^{\oplus}$ position in the refinements (Table 2).

Dipotassium Dihydrogen 1,3,5,7-Adamantanetetracarboxylate (**2**): $C_{14}H_{14}O_8K_2$, $M_r = 388.46$. — Crystallization: **1** was half-neutralized with 0.1 n aqueous KOH and the water slowly evaporated. As with **3**, several (probably three) types of crystals formed simultaneously, and those of the dipotassium salt **2** were again characterized by their partially dendritic appearance. — Crystal data of **2** (isomorphism with disodium salt **3**; see above for crystal symmetry data): $a = 10.282(2)$, $c = 13.895(2)$ Å; $\varrho_{calcd.} = 1.756$ gcm^{-3}, $\varrho_{found} = 1.74$ gcm^{-3} (CCl_4/CH_2Br_2, flotation). Intensity measurements, structure analysis, and refinement as in the case of **3**; $R = 0.102$, $R_w = 0.115$ [$\Theta_{max} = 30°$, 456 reflections with $F_o > 4\ \sigma(F_o)$,

Table 3. Atomic coordinates, numbering, weights (g), and equivalent isotropic temperature factors [$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$] of **6**; x, y, z of Na, C, O multiplied by 10^4, other quantities by 10^3 (O_W, H_W: oxygen and hydrogen atoms of partially disordered water; H_W parameters assumed)

	x	y	z	g	U_{eq}
Na	6753(2)	5915(2)	984(2)	1000	74(1)
C(1)	5465(4)	3520(3)	3118(3)	1000	27(1)
C(2)	6462(4)	3056(4)	3752(3)	1000	32(1)
C(3)	5000	2500	2505(4)	500	30(1)
C(4)	5888(4)	4535(4)	2483(3)	1000	35(1)
O(1)	5185(3)	4874(3)	1833(2)	1000	50(1)
O(2)	6863(3)	5006(3)	2607(2)	1000	52(1)
O_w	5153(4)	6322(3)	-88(3)	1000	74(1)
H(2A)	683(4)	368(4)	406(3)	1000	38(13)
H(2B)	709(4)	284(4)	342(3)	1000	39(11)
H(3)	443(3)	271(3)	212(2)	1000	22(9)
$H_w(1)$	504	594	-64	1000	150
$H_w(2)$	505	711	-9	500	150
$H_w(3)$	506	560	17	500	150

bridging hydrogen atoms fixed asymmetrically with half-weights on the O $\cdots$ O interconnecting line]. The relatively high R value may be due to the partial disorder phenomena and the limited crystal quality; this holds similarly for **3** (see above). The refined atomic coordinates and temperature factor coefficients are listed in Table 1[14]. It is noted that X-ray photographs (precession films) of the dipotassium salt **2** did not reveal any peculiarities like super-lattice reflections and thus confirm the partially disordered character of the structure. Furthermore, structure solutions and refinements of **2** were attempted in the polar subgroup $P4_2bc$ (No. 106). However, no evidence could be found to support this (interesting) symmetry reduction.

Tetrasodium 1,3,5,7-Adamantanetetracarboxylate Tetrahydrate (**6**): $C_{14}H_{12}O_8Na_4 \cdot 4H_2O$, $M_r = 472.27$. — Tetragonal crystals of uncharacteristic shape (crystallization, see disodium salt **3** above). — Crystal data: space group $I4_1/a$ (No. 88), $Z = 4$, $a = 11.273(3)$, $c = 14.119(4)$ Å; $\varrho_{calcd.} = 1.748$ gcm^{-3}, $\varrho_{found} = 1.75$ gcm^{-3} (CCl$_4$/CH$_2$Br$_2$, flotation); measuring conditions, structure analysis, and refinement similar as for **3** (C, O, Na anisotropically, adamantane hydrogen atoms isotropically refined; positions of the H atoms of the hydrogen bonds constructed and considered only in the structure factor calculations, with half-weights if required by partial disorder); 584 reflections with $F_o > 4\sigma(F_o)$, $R = 0.064$, $R_w = 0.075$. The refined atomic coordinates and temperature factor coefficients are listed in Table 3[14].

[1] O. Ermer, *J. Am. Chem. Soc.* **110** (1988) 3747.

[2] O. Ermer, A. Eling, *Angew. Chem.* **100** (1988) 856; *Angew. Chem. Int. Ed. Engl.* **27** (1988) 829.

[3] O. Ermer, L. Lindenberg, *Helv. Chim. Acta* **71** (1988) 1084.

[4] [4a] J. C. Speakman, *Structure and Bonding (Berlin)* **12** (1972) 141. — [4b] J. Emsley, *Chem. Soc. Rev.* **9** (1980) 91. — [4c] See, however: C. L. Perrin, J. D. Thoburn, *J. Am. Chem. Soc.* **111** (1989) 8010.

[5] L. Pauling: *The Nature of the Chemical Bond*, Cornell University Press, Ithaca 1960.

[6] O. Ermer, L. Lindenberg, results to be published.

[7] See, for example: J. A. Ibers, L. J. Pace, J. Martinsen, B. M. Hoffman, *Struct. Bonding (Berlin)* **50** (1982) 1. — Interestingly, a nickel complex of an octamethyltetrabenzoporphyrin, partially oxidized by iodine, of composition $C_{44}H_{36}(I_3)_{0.36}N_4Ni$ also crystallizes in space group $P4_2/nbc$ with 4 formula units per unit cell: T. E. Phillips. R. P. Scaringe, B. M. Hoffman, J. A. Ibers, *J. Am. Chem. Soc.* **102** (1980) 3435. The crystal structure of this nickel complex, which displays metal-like conductivity, is completely analogous to that of **2** and **3** with the dihydrogen tetracarbox-ylate anions replaced by cationic stacks of porphyrinatonickel moieties (crystallographic S_4 symmetry, stacking distance 3.778 Å) and the alkali cations by anionic (disordered) I_3^- col-umns. Accordingly, the crystal structure of the nickel porphyrin complex may formally also be described in terms of a fourfold diamond architecture, but this is physically rather meaningless due to the absence of any preferred diamondoid interactions (like, e. g., hydrogen bonds as in **2** and **3**) between the porphyrin systems.

[8] J. D. Watson, F. H. C. Crick, *Nature (London)* **171** (1953) 737.

[9] G. E. Bacon, R. S. Pease, *Proc. R. Soc. London, Ser. A,* **220** (1953) 397, **230** (1955) 359. See also: J. C. Burfoot, G. W. Taylor, *Polar Dielectrics and their Applications*, McMillan Press, London 1979.

[10] W. Saenger, C. Betzel, B. Hingerty, G. M. Brown, *Nature (London)* **296** (1982) 581.

[11] [11a] H. M. Powell, *J. Chem. Soc.* **1948** 61. — [11b] G. A. Jeffrey, *Acc. Chem. Res.* **2** (1969) 344.

[12] [12a] H. Stetter, O.-E. Bänder, W. Neumann, *Chem. Ber.* **89** (1956) 1922. — [12b] S. Landa, Z. Kamycek, *Coll. Czech. Chem. Commun.* **24** (1959) 4004.

[13] [13a] B. A. Frenz, *SDP, Structure Determination Package*, Enraf-Nonius, Delft, Holland, 1978. — [13b] G. M. Sheldrick, *SHELX 76, Program for Crystal Structure Determination*, University of Cambridge, England, 1976.

[14] Further details of the crystal structure investigations are avail-able on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, F.R.G., on quoting the de-pository number CSD-54290, the names of the authors, and the journal citation.

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