TOPOLOGICAL CORRESPONDENCE BETWEEN CRYSTAL STRUCTURE OF 2,4,6-TRIMETHYLBENZENE-1,3,5-TRIS(METHANAMINIUM) 2,4,6-TRIMETHYLBENZENE-1,3,5-TRIACETATE AND CESIUM CHLORIDE

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Solid-state self-assembly of 2,4,6-trimethylbenzene-1,3,5-tris(methanaminium) 2,4,6-trimethylbenzene-1,3,5-triacetate is mediated by hydrogen bonding. It gives rise to three-dimensional network of hydrogen bonds in which each trication is coordinated with eight trianions and *vice versa*. The resulting crystal structure topologically corresponds to the simple inorganic cesium chloride type.

Key words: Carboxylic acids; Amines; Hydrogen bonds; Crystal engineering; X-Ray diffraction; Supramolecular chemistry; Self assembly.

Majority of *inorganic ionic* compounds of the M^+X^- type exists in the cesium chloride or sodium chloride crystal type, each ion in the former structure being coordinated with eight, whereas in the latter with six counter-ions (Figs 1a, 1b). For a given salt, the maximum coordination number is preferred, which allows a close contact between opposite-charge ions without compressing ions of the same charge. Relative size of the counter-ions is the decisive factor. A simple geometric analysis[1] shows that the ratio of the radii of the oppositely charged ions, r^-/r^+ must be equal or less than 1.37 in order to secure effective coordination of the anion with eight cations, and *vice versa*. In principle, an analogous situation can be also expected for the corresponding polyvalent salts, $M^{(n+)}X^{(n-)}$, provided that the participating ions possess spherical symmetry and uniform charge distribution.

Such a stipulation does not hold for *organic ionic* compounds since they usually do not exhibit either spherical symmetry or uniform charge distribution. Formation of crystal structures of such compounds is accordingly controlled by other (more complex) rules and forces. Does it, however, exclude analogies with simple crystal structures of the inorganic salts? Desiraju, in his penetrating study[2a] on crystal engineering pointed out that *any* organic crystal (ionic as well as non-ionic) may be depicted as a network with the molecules as nodes and showed, at the same time, that the next logical step in this visualization is to search for the topological correspondences with its inorganic counterpart. So far, only one pertinent example of such correspondence has been reported[2b].

In this paper, we wish to report on an unexpected case of a topological correspondence between crystal structure of a complex triple-charged organic and a simple single-charged inorganic salt.

RESULTS AND DISCUSSION

Self-assembly of organic salts in crystal is often organized by ionic hydrogen bonding[3–5] allowing the simultaneous use of directional hydrogen bonds and less directional electrostatic interaction between the opposite-charge units. As a part of our interest in this self-assembly, we have examined the hydrogen bonding pattern in the organic salt **1** arising by triple proton transfer from 2,4,6-trimethylbenzene-1,3,5-triacetic acid **2** to 2,4,6-trimethylbenzene-1,3,5-tris(methanamine) **3** in the solid state. The starting compounds **2** and **3** were prepared from the corresponding tribromide **6** by simple procedures outlined in Scheme 1.

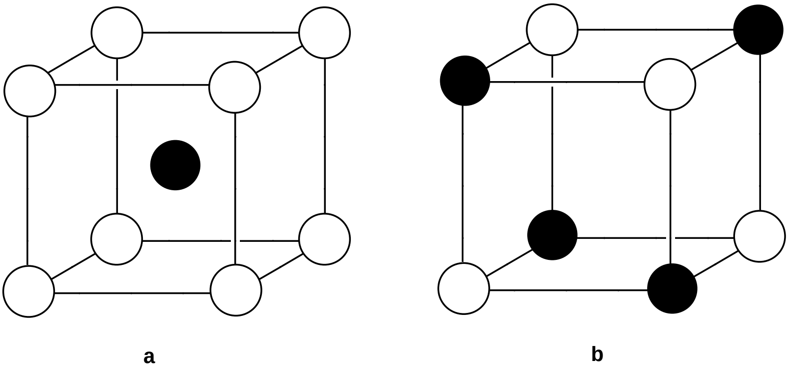
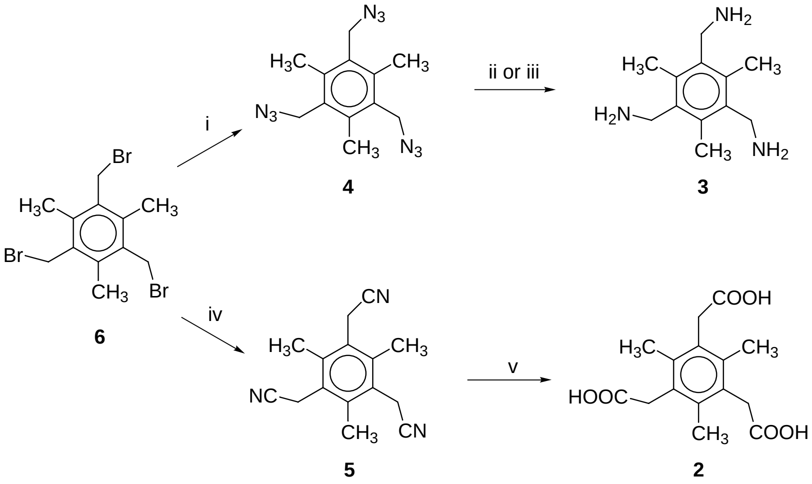


FIG. 1
Cesium chloride (a) and sodium chloride (b) crystal type



i : NaN_3, DMSO
ii : PPh_3; NH_4OH; HCl; DOWEX OH^-
iii : H_2, Pd/C
iv : NaCN, DMSO
v : NaOH, H_2O/EtOH; HCl

SCHEME 1

Mixing of equimolar amount of **2** and **3** in water followed by crystallization of the resulting precipitate from aqueous ethanol gave the triple-charged salt **1**. According to elemental analysis supported by NMR spectra and X-ray data, the obtained salt **1** corresponds to the formula $C_{12}H_{24}N_3{}^{3+}\cdot C_{15}H_{15}O_6{}^{3-}\cdot 3H_2O\cdot 0.5C_2H_5OH$. X-Ray diffraction analysis of the single crystal confirms that all carboxylic groups are ionized and all amino groups are protonized.

Molecular Structure

Looking at the molecular structure of both participating triple-charged ions in a crystal of salt **1** (Fig. 2), one finds nothing unusual with the bond distances and angles. The carbon atoms of the benzene rings plus the directly bonded carbon atoms are almost exactly planar and the ammonium as well as the carboxylate groups are distributed in the "up-up-down" manner, taken relatively to the corresponding benzene ring. The geometry of the positively charged nitrogen atoms is roughly tetrahedral, supporting the formulation of the trication. In the trianion, the metric parameters of the carboxy groups are close, but not identical, to those of the isolated dissociated carboxyl[6]. The difference may be due to the perturbation caused by hydrogen bonding.

Hydrogen Bonding Pattern

Interaction between the opposite triple-charged ions resulting from **2** and **3** in the salt crystal is mediated by hydrogen bonding. There is a variety of hydrogen bonds summarized in Table I. Although some of them should be taken with caution due to the problem associated with the hydrogen atoms at N1 and, in part, also on O9, most of them are unambiguous. Links between the ammonium and carboxy groups are either direct or by means of water molecules. The direct $^{+}\text{NH}\cdots\text{O}$ links (Fig. 3) are markedly asymmetric, in accordance with the charge of the participating ions. The shortest hydrogen-bond contacts between the opposite ions give rise, *via* the $^{+}\text{NH}\cdots\text{O}$ bonds, to zig-zag ladders which are placed in parallel in *xz* plane (Fig. 4) and stacked in the perpendicular plane (Fig. 5). A close analysis reveals that the neighbouring ladders are linked by longer hydrogen bond interactions ($^{+}\text{NH}\cdots\text{O}$, $^{+}\text{NH}\cdots\text{OH}_2\cdots\text{OH}_2\cdots{}^{-}\text{O}_2\text{C}$, $^{+}\text{NH}\cdots\text{OH}_2\cdots\text{C}_2\text{H}_5\text{OH}\cdots{}^{-}\text{O}_2\text{C}$). This gives rise to the three-dimensional network of hydrogen bonds (Fig. 6) in which each trication is coordinated with eight trianions and *vice versa* (Fig. 7). In this way, the situation closely resembles the crystal packing of cesium chloride (Fig. 1a).

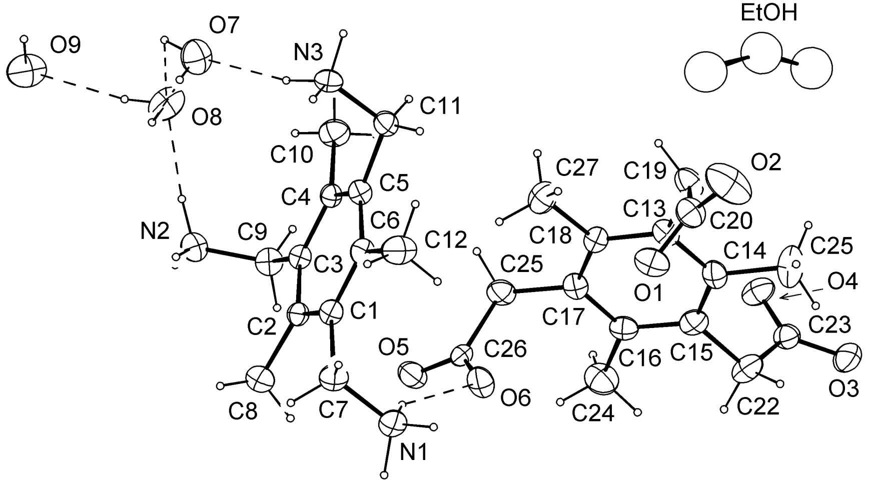


FIG. 2
Single-crystal molecular structure of salt **1** with atom labelling

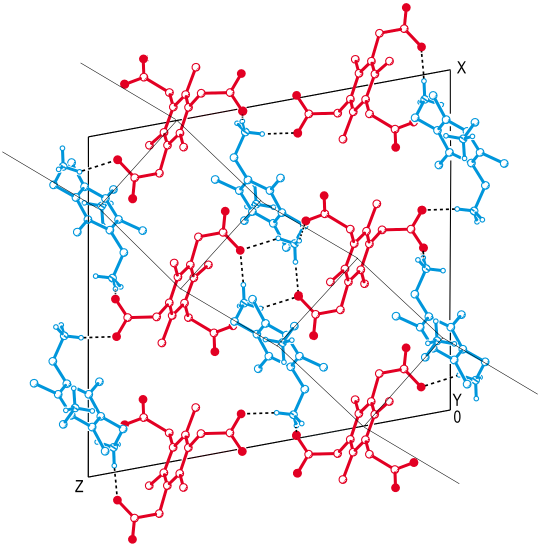


FIG. 3
Direct ionic hydrogen bonds $–^{+}NH_3\cdots^{-}OOC–$ in the crystal structure of salt **1**

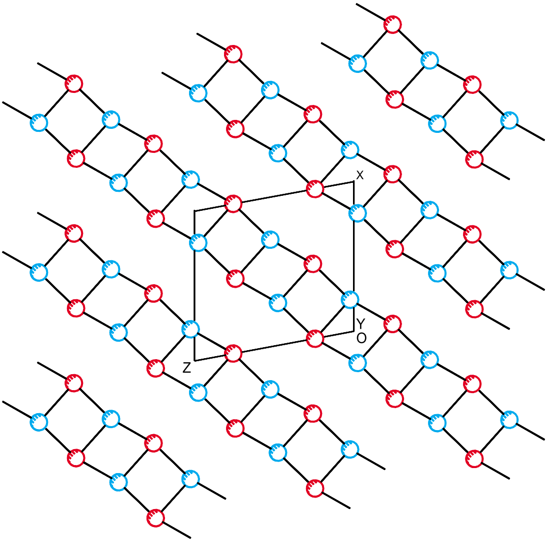


FIG. 4
Schematic representation of zig-zag ladders formed by the shortest ionic hydrogen bonds (*cf*. Fig. 3) in *xz* plane. The opposite triple-charged ions are represented by blue and red spheres

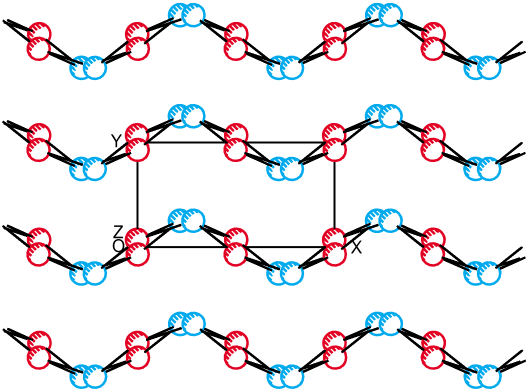


FIG. 5
Stacking of zig-zag ladders in perpendicular (*xy*) plane

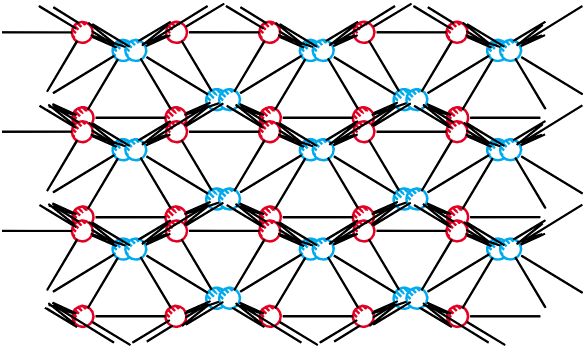


FIG. 6
Linking of the neighbouring ladders by solvent molecules (H_2O, EtOH) gives rise to the three-dimensional network of hydrogen bonds

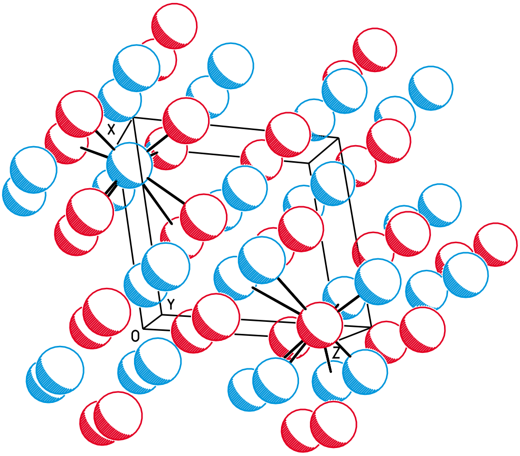


FIG. 7

In the resulting three-dimensional network, each trication is coordinated with eight trianions and *vice versa*

EXPERIMENTAL

1,3,5-Tris(azidomethyl)-2,4,6-trimethylbenzene (**4**)

Sodium azide (5.2 g, 80 mmol) was added to a solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene **6** (ref.[7]; 7.98 g, 20 mmol) in dimethylformamide (100 ml). The mixture was stirred at room temperature for 5 h and poured into cold water (400 ml). The resulting precipitate was filtered off and washed with water. After drying it was crystallized from methanol; yield 5.5 g (96%), m.p. 64–65 °C. ^{1}H NMR ($CDCl_3$): 4.45 s, 6 H (CH_2); 2.48 s, 9 H (CH_3). EI-MS, *m/z* (rel.%): 285 (M^+, 43), 243 (72), 200 (100), 185 (38), 172 (63), 158 (77), 157 (84), 144 (66), 130 (57), 115 (40), 91 (44), 77 (41), 65 (28), 51 (28), 39 (34). (*Caution: Explosion occurred in the course of elemental analysis*.)

2,4,6-Trimethylbenzene-1,3,5-tris(methanamine) (**3**)

Procedure A (trihydrochloride). Triphenylphosphine (15.17 g, 57.8 mmol) was slowly added to a stirred solution of triazide **4** (5.5 g, 19.3 mmol) in tetrahydrofurane (150 ml). After 2 h, concentrated ammonium hydroxide (22 ml) was added, the mixture was stirred for 15 h and evaporated to dryness. The residue was suspended in water (500 ml) and neutralized with 1 M HCl to pH 5. The suspension was extracted with toluene (3 × 250 ml), the aqueous layer was filtered through cellite and evaporated to dryness; yield 5.8 g (95%). ^{1}H NMR (D_2O): 4.24 s, 6 H (CH_2); 2.50 s, 9 H (CH_3). Positive spectrum FAB-MS, *m/z*: 208 ($[MH]^+$ – 3 HCl). For $C_{12}H_{24}Cl_3N_3$ (316.7) calculated: 45.51% C, 7.64% H, 13.27% N; found: 45.13% C, 7.95% H, 12.95% N.

Procedure B (free base). A gentle stream of hydrogen was bubbled into a mixture of triazide **4** (2.85 g, 10 mmol) and palladium catalyst (10% Pd/C, 50 mg) in methanol (30 ml). After the slightly exothermic reaction ceased (approximately 40 min), the catalyst was removed by filtration, the reaction mixture was evaporated to dryness and the solid residue was dissolved in hot toluene (50 ml). After cooling, the crystals were collected and dried *in vacuo*. Yield 1.87 g (90.2%), m.p. 143–145 °C. ^{1}H NMR ($CDCl_3$): 3.93 s, 6 H (CH_2); 2.46 s, 9 H (CH_3); 1.27 br s, 6 H (NH_2). EI-MS, *m/z* (rel.%): 207 (M^+, 6), 191 (13), 190 (100), 175 (45), 171(14), 170 (20), 158 (49), 156 (13), 144 (10), 131 (10), 91 (10). For $C_{12}H_{21}N_3$ (207.3) calculated: 69.52% C, 10.21% H, 20.27% N; found: 69.52% C, 10.27% H, 19.94% N.

1,3,5-Tris(cyanomethyl)-2,4,6-trimethylbenzene (**5**)

Potassium cyanide (31.24 g, 451 mmol) was treated with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene **6** (ref.[7]; 39.9 g, 100 mmol) in dimethyl sulfoxide (300 ml) at room temperature for 24 h. Usual work-up and crystallization (ethanol) afforded 19.9 g (84%) of

TABLE I
Possible hydrogen bonds. Symmetry code: i, 1 – *x*, –*y*, 1 – *z*; ii, 0.5 – *x*, *y*, 0.5 – *z*; iii, *x* – 0.5, –*y*, *z* + 0.5; iv, 1 – *x*, 1 – *y*, 1 – *z*; v, *x*, 1 + *y*, *z*; vi, 0.5 – *x*, 1 + *y*, 0.5 – *z*; vii, 1 – *x*, *y*, *z*; viii, 1.5 – *x*, 1 + *y*, 0.5 – *z*

Atom			Distance, Å			Angle, ° X–H···Y
X	H	Y	X–H	H···Y	X···Y	
N1	H1NA	$O1^{i}$	0.89	1.93	2.741(8)	150
N1	H1NB	O6	0.89	1.98	2.830(7)	159
N1	H2NC	$O6^{i}$	0.89	1.92	2.801(6)	170
N2	H2NA	$O3^{ii}$	0.74(7)	2.11(8)	2.76(1)	146(7)
N2	H2NB	O8	1.0(1)	1.9(1)	2.82(1)	163(8)
N2	H2NC	$O4^{iii}$	0.92(9)	1.86(10)	2.777(9)	173(7)
N3	H3NA	O7	1.00(8)	2.04(8)	3.013(8)	166(6)
N3	H3NB	$O1^{iv}$	0.88(6)	1.91(6)	2.752(8)	160(5)
N3	H3NC	$O5^{v}$	0.93(7)	1.73(8)	2.649(9)	169(6)
O7	H7OA	$O9^{iv}$	0.81	1.91	2.720(8)	177.2
O7	H7OB	$O9^{vi}$	0.81	2.4	2.855(7)	147.2
O8	H8OA	O7	0.81	2.10	2.862(8)	156.7
O8	H8OB	$O9^{vii}$	0.81	2.08	2.880(8)	172.0
O9	H9OA	O2	0.81	1.94	2.744(8)	172.7
O9	H9OB	$O4^{viii}$	0.81	1.99	2.705(8)	147.3

the product, m.p. 256–258 °C (ref.[9] 251–253 °C). ^{1}H NMR ($CDCl_3$): 3.74 s, 6 H (CH_2); 2.46 s, 9 H (CH_3). EI-MS, *m/z* (rel. %): 237 (M^+, 50), 210 (100), 197 (35), 183 (12), 170 (18), 154 (7), 128 (11), 115 (11), 91 (5), 77 (6), 63 (4), 51 (5), 39 (6). IR (KBr): 2 978 m, 2 957 m (ν_{as} CH_3); 2 882 w sh (ν_s CH_3); 2 248 s (ν CN); 1 574 w, 1 471 w sh (ν ring); 1 454 m (δ_{as} CH_3); 1 428 vs (β_s CH_2); 1 386 m (δ_s CH_3); 1 311 w (γ_s CH_2); 1 298 w, 1 101 w, 1 023 m (aromatics); 1 232 w (γ_{as} CH_2); 935 w, 922 w, 907 w (ν C–CN); 803 m (β_{as} CH_2). For $C_{15}H_{15}N_3$ (237.3) calculated: 75.92% C, 6.37% H, 17.71% N; found: 75.62% C, 6.43% H, 17.92% N.

2,4,6-Trimethylbenzene-1,3,5-triacetic Acid (**2**)

The tris(cyanomethyl) derivative **5** (6.7 g, 28.2 mmol) was heated under reflux with 20% aqueous sodium hydroxide in ethanol (28 ml) for 14 h. The reaction mixture was acidified with concentrated hydrochloric acid, the precipitate was filtered off, washed with water and recrystallized from water. Yield 6.82 g (82%), m.p. 282–284 °C (ref.[5] 283–285 °C). ^{1}H NMR (CD_3SOCD_3): 12.27 s, 3 H (COOH); 3.63 s, 6 H (CH_2); 2.16 s, 9 H (CH_3). EI-MS, *m/z* (rel.%): 294 (M^+, 4), 256 (22), 213 (8), 185 (8), 167 (9), 149 (28), 129 (21), 111 (14), 97 (28), 83 (34), 69 (51), 57 (93), 43 (100). IR (KBr): 3 479 w (ν OH, COOH monomer); 3 073 s, 3 002 s (ν OH, COOH dimer); 2 975 s (ν_{as} CH_3); 2 893 s sh (ν_s CH_3); 2 738 s, 2 645 s, 2 548 m (dimer); 1 697 vvs, 1 655 s (ν C=O); 1 572 w, 1 477 m sh (ν ring); 1 458 m (δ_{as} CH_3); 1 438 m sh (β_s CH_2); 1 412 s, 1 288 s, 1 243 s (ν C–O + δ COH, COOH dimer); 1 393 s, 1 378 s sh (δ_s CH_3); 1 323 m (γ_s CH_2); 1 227 s (γ_{as} CH_2); 1 303 s sh, 1 189 s, 1 243 s (aromatics); 1 075 w, 1 066 w (δ_{as} CH_3); 930 s br (γ COH, COOH dimer); 799 w (β_{as} CH_2). For $C_{15}H_{18}O_6$ (294.3) calculated: 61.22% C, 6.16% H; found: 60.96% C, 6.14% H.

X-Ray Diffraction Analysis

Single crystal X-ray diffraction data: $C_{12}H_{24}N_3^{3+}\cdot C_{15}H_{15}O_6^{3-}\cdot 3H_2O\cdot 0.5C_2H_5OH$, M.w. 578.7, monoclinic, space group *P2/n* (non-standard setting of *P2/c*, No. 13), a = 17.476(1) Å, b = 9.103(2) Å, c = 18.908(2) Å, β = 100.583(7)°, V = 2 957.3(5) Å^{-3}, Z = 4, D_c = 1.300 g cm^{-3}, $F(000)$ = 1 252. A prismatic crystal of the dimensions 0.2 × 0.1 × 0.3 mm (grown from 20% aqueous ethanol) was measured at 293 K on a CAD4 diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Absorption was neglected (μ = 0.10 mm^{-1}). The lattice parameters were determined from 25 reflections in the 12–13° θ-range. The intensities of reflections were measured by θ–2θ scan between h 〈–16,16〉, k 〈0,8〉, l 〈0,18〉. Three standard reflections monitored during the measurement in 1 h intervals showed an intensity variation of 2%. From 3 090 measured reflections, 2 097 were unique (R_{int} = 0.0513) and 1 553 were regarded as "observed" according to the $I \geq 2\sigma(I)$ criterion. The structure was solved by direct methods[9] (SHELXS86) and refined by SHELXL93 (ref.[10]) using a full-matrix least squares procedure based on F^2. There remained significant regions of electron density on the difference map, which were interpreted as one half of disordered ethanol per formula unit (originated from the solvent used for obtaining the single crystal). The disorder was modeled with two positions of ethanol related by slightly mutually displaced (by 0.45 Å) central carbon atoms and terminal atoms of 0.5 relative occupancy or carbon and/or oxygen, *i.e.*, these atoms are interchanged in the two positions. This model appears justified since (i) it leads to considerable lowering of the *R*-factor, (ii) the resulting metric parameters of ethanol are quite reasonable: the central-terminal interatomic distance (*i.e.*, the mean of C–C and C–O) is 1.43 Å and the bond angle on the central carbon is 122°, (iii) the presence of ethanol was confirmed by NMR spectroscopy. From the crystallographic point of view, its molecule is located in a channel within the structure displaying no close intermolecular contacts, hence the disorder. No attempt was made to locate the hydrogen atoms of ethanol. All other hydrogens were clearly visible in the difference map. They were refined isotropically except for the hydrogens at N1 and for those in water molecules which, for unknown reasons, behaved erratically on refinement. These hydrogen atoms were eventually fixed at the positions found from the difference map and given the isotropic temperature factor of N1 and of water oxygens multiplied by 1.2. All the non-hydrogen atoms were refined anisotropically. The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (0.104P)^2 + 1.670P]$, $P = (F_o^2 + 2F_c^2)/3$. This model converged for 417 parameters to $R = 0.056$, $R_w = 0.145$, $GOF = 1.066$ and $(\Delta/\sigma)_{max} = \pm0.02$ for non-H atoms. The final difference electron density map displayed extreme values of 0.82 e Å^{-3} (near the ethanol molecule) and –0.34 e Å^{-3}. The tables of observed and calculated structure factors and of anisotropic displacement parameters, as well as the standard CIF file produced by SHELXL93, can be obtained from the author (I. C.) upon request. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-145738. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

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REFERENCES AND NOTES

1. Cotton F. A., Wilkinson G.: *Advanced Inorganic Chemistry*, 2nd ed. Wiley, New York 1966.
2. a) Desiraju G. R.: *Chem. Commun.* **1997**, 1475; b) Reddy D. S., Craig D. C., Desiraju G. R.: *J. Chem. Soc., Chem. Commun.* **1995**, 339.
3. a) Hosseini M. W., Brand G., Schaeffer P., Ruppert R., De Cian A., Fischer J.: *Tetrahedron Lett.* **1996**, *37*, 1405; b) Felix O., Hosseini M. W., De Cian A., Fischer J.: *Tetrahedron Lett.* **1997**, *38*, 1933; c) Felix O., Hosseini M. W., De Cian A., Fischer J.: *Tetrahedron Lett.* **1997**, *38*, 1755; d) Hosseini M. W., Ruppert R., Schaeffer P., De Cian A., Kyritsakas N., Fischer J.: *J. Chem. Soc., Chem. Commun.* **1994**, 2135; e) Felix O., Hosseini M. W., De Cian A., Fischer J.: *Chem. Commun.* **2000**, 281; f) Felix O., Hosseini M. W., De Cian A., Fischer J.: *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 102.
4. a) Mascal M., Fallon P. S., Batsanov A. S., Heywood B. R., Champ S., Colghough M.: *J. Chem. Soc., Chem. Commun.* **1995**, 805; b) Grawe T., Schrader T., Gurrath M., Kraft A., Osterod F.: *Org. Lett.* **2000**, *2*, 29; c) Kraft A.: *J. Chem. Soc., Perkin Trans. 1* **1999**, 705.
5. Melendez R. E., Zaworotko M.: *Supramol. Chem.* **1997**, *8*, 157.
6. Bortwick P. W.: *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 628.
7. Závada J., Pánková M., Holý P., Tichý M.: *Synthesis* **1994**, 1132.
8. Nakanishi M., Kuriyama T., Yuki H.: Japan 13096 (1967); *Chem. Abstr.* **1967**, *67*, 108458.
9. Sheldrick G. M.: *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **1990**, *46*, 467.
10. Sheldrick G. M.: *SHELXL93, Program for Crystal Structure Refinement from Diffraction Data*. University of Göttingen, Göttingen 1995.