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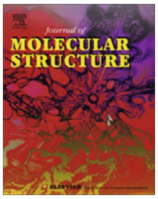

Crystals of the Kemp's triacid salts – Part VI: Supramolecular architecture in the crystal of Kemp's triacid with tris(2-aminoethyl)amine

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ABSTRACT

A complex crystal [H_3KTA–TAEA–EA] is composed of triply deprotonated Kemp's triacid molecule (KTA^{3-}), triply protonated tris(2-aminoethyl)amine (H_3TAEA^{3+}) molecule and one ethanol molecule (EA) as a solvate. The ring of the (KTA^{3-}) trianion exhibits an uncommon twisted boat conformation with two carboxylic groups in the axial positions and one in the equatorial position. In the crystal each KTA^{3-} trianion is hydrogen-bonded with four H_3TAEA^{3+} molecules forming three-dimensional hydrogen-bonded network within the supramolecular complex. The ethanol molecules form a uncommon dimer bonded by very weak tandem hydrogen bonds. The IR spectrum of the crystal is consistent with the results obtained by the X-ray study and provides spectroscopic evidence for the crystal formation.

1. Introduction

Crystal engineering has provided chemists with a useful paradigm for the rational design of solid-state structures [1–3]. In particular, self-assembly of preselected molecular building blocks can yield designed supramolecular structure in one-pot synthesis. Crystal engineering and the design of solid-state architectures are of considerable contemporary interest from the point of view of potential applications of functional materials. In this context several research groups [4–15] have studied the crystalline molecular complexes between carboxylic acid and several amines including hydrogen bonds.

Nowadays, there is growing interest in supramolecular chemistry of tripodal ligands with *C*3 topology. Tris(aminoethyl)amine (TAEA) (Scheme 1) is a well-known representative of this group of ligand commonly used and commercially available [16–18].

The tricarboxylic acid such as Kemp's triacid (*cis,cis*-l,3,5-trimethylcyclohexane-l,3,5-tricarboxylic acid, H_3KTA) (Scheme 1) is considered an interesting agent in designing molecular system for crystal engineering and for studies of three-dimensional hydrogen-bonded networks within the supramolecular complexes [19].

In our previous papers we reported on the molecular structures of several crystals of H_3KTA with 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) [20], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [21], tetramethylguanidine (TMG) [22], 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) [23] and melamine (MEL) [24]. It was demonstrated that the chair conformation of the KTA molecule was retained also in its salts in which monoanion or dianion of Kemp triacid was present. In these crystals the multiple charge-assisted $O—H\cdots O^-$ intramolecular and $O—H\cdots O^-$, $N^+—H\cdots O^-$ intermolecular hydrogen bonds are the main interactions stabilizing their structures.

As a continuation of these studies we synthesized a new hydrogen-bonded crystal formed by Kemp's triacid (H_3KTA) and tris(2-aminoethyl)amine (TAEA) and studied its structure by X-ray diffraction and FT-IR spectroscopy.

2. Experimental

All materials were obtained from Sigma–Aldrich or Fluka and used without any further purification.

2.1. Synthesis of H_3KTA–TAEA–EA complex

A 1:1 mixture of H_3KTA and TAEA was dissolved in hot ethanol (EA) and left at room temperature. After a few days transparent colourless crystals were formed.

2.2. X-ray measurements

A colourless single crystal of $[(C_{12}H_{15}O_6)^{3-} \cdot (C_6H_{21}N_4)^{3+} \cdot (C_2H_5OH)]$ of the size of 0.27 × 0.24 × 0.21 mm was measured on a

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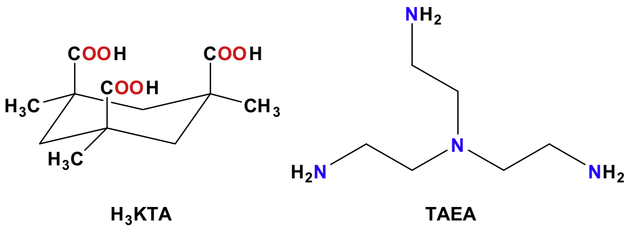

Scheme 1. The formula of H_3KTA and TAEA.

KUMA KM-4 diffractometer equipped with two-dimensional area CCD detector. The graphite monochromatized Mo Kα (λ = 0.71073 Å) radiation was used for data collection. The lattice parameters were refined by the least-squares methods on the basis of 1262 reflections. 157709 reflections (5558 independent, R_{int} = 0.0385) were measured up to 56° in 2θ covering over 99% of the Ewald sphere. Data collection was made using the CrysAlis CCD program [25], integration, scaling of the reflections and absorption corrections were performed with the CrysAlis Red program [25]. The structure was solved by direct methods using SHELXS-97 and refined using the SHELXL-97 program [26]. The hydrogen atoms joined to the carbon atoms were constrained. The H atoms involved in the hydrogen bonds were refined. The final differences Fourier maps showed no peaks of chemical significance. The largest peaks on the final $\Delta\rho$ map were +0.359 and −0.306 e Å^{-3}. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Visualisation of the structure was made with the Diamond 3.0 program [27].

2.3. FT-IR measurements

The FT-IR spectra of H_3KTA–TAEA–EA crystals, TAEA and H_3KTA were recorded in the mid infrared region in nujol/fluorolube mulls at 300 K. The spectra were taken with an IFS 113v FT-IR spectrophotometer (Bruker, Karlsruhe) equipped with a DTGS detector; resolution 2 cm^{-1}, NSS = 64. The Happ–Genzel apodization function was used.

Table 1
Crystallographic data and structure refinement parameters.

Empirical formula	$(C_{12}H_{15}O_6)(C_6H_{21}N_4)(C_2H_6O)$
Formula weight (g mol^{-1})	450.58
Crystal system, space group	Triclinic, $P-1$
a, b, c (Å)	8.811(2), 11.348(2), 12.288(3)
α, β, γ (°)	102.04(1), 103.64(1), 93.75(1)
V (Å^3)	1159.2(4)
Z	2
D_{calc}/D_{obs} (g cm^{-3})	1.291/1.29
μ (mm^{-1})	0.097
F(0 0 0)	492
Crystal size (mm)	0.27 × 0.24 × 0.21
Radiation type, wavelength, λ (Å)	Mo Kα, 0.71073
Temperature (K)	295(2)
θ range (°)	2.84–28.0
Absorption correction	Numerical, CrysAlis Red [25]
T_{min}/T_{max}	0.9755/0.9806
Reflections collected/unique/observed	15709/5558/2780
R_{int}	0.0385
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0529
$wR(F^2$ all reflections)	0.1192
Goodness-of-fit, S	1.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.359, −0.306

$wR = \{\Sigma\,[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$; $w^{-1} = (\sigma^2(F_o^2) + (0.0530P)^2)$ where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

3.1. Description of the structure

The Kemp triacid ($C_6H_3(CH_3)_3(COOH)_3$) has three ionisable carboxyl groups and it can form mono-, di- and tri-deprotonated salts. The molecular structure of the neutral Kemp triacid molecule in the crystal exhibits chair conformation of the skeletal cyclohexane ring with *cis,cis* triaxial arrangement of the carboxyl groups [28–31]. In several crystals of single H_2KTA^- and double deprotonated $HKTA^{2-}$ salts that have been structurally characterised [20–24,32–34] the chair conformation of the cyclohexane ring and tri-

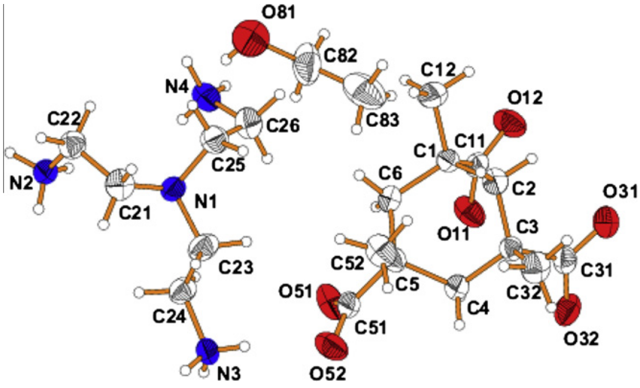

Fig. 1. View of the asymmetric unit of the H_3KTA–TAEA–EA crystal with the labelling of the atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary size.

Table 2
Selected geometric parameters (Å, °).

C11—O12	1.241(2)	C11—O11	1.264(2)
C31—O31	1.251(2)	C31—O32	1.259(2)
C51—O51	1.252(2)	C51—O52	1.260(2)
O12—C11—O11	122.27(17)	O31—C31—O32	123.44(17)
O51—C51—O52	120.95(18)		
C1—C2—C3—C4	−33.3(2)	C2—C3—C4—C5	−23.1(2)
C3—C4—C5—C6	57.6(2)	C4—C5—C6—C1	−35.4(2)
C5—C6—C1—C2	−16.5(2)	C6—C1—C2—C3	53.7(2)
N1—C25	1.456(2)	N1—C21	1.464(2)
N1—C23	1.474(2)	C22—N2	1.481(2)
C24—N3	1.495(2)	C26—N4	1.480(3)
C25—N1—C21	112.33(14)	C25—N1—C23	111.31(14)
C21—N1—C23	112.49(15)		
N1—C21—C22—N2	68.7(2)	N1—C23—C24—N3	−172.5(2)
N1—C25—C26—N4	67.5(2)		

Table 3
Geometric parameters of the hydrogen bonds (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H23···O11^{i}	0.92(2)	1.87(2)	2.792(2)	177(2)
N2—H23···O12^{i}	0.92(2)	2.51(2)	3.134(2)	125(2)
N2—H24···O32^{ii}	0.92(2)	1.88(2)	2.768(2)	163(2)
N2—H25···O12^{iii}	0.85(2)	1.92(2)	2.762(2)	172(2)
N3—H31···O51	0.84(2)	2.20(2)	2.972(2)	153(2)
N3—H31···O52	0.84(2)	2.51(2)	3.258(2)	150(2)
N3—H32···O32^{iv}	0.87(2)	1.87(2)	2.728(2)	167(2)
N3—H33···O31^{iii}	0.95(2)	1.83(2)	2.761(2)	166(2)
N4—H43···O11^{i}	0.77(2)	1.99(2)	2.724(2)	162(3)
N4—H44···O51^{i}	0.96(2)	1.76(2)	2.719(2)	175(2)
N4—H45···O52^{v}	0.99(2)	1.77(2)	2.745(2)	167(2)
O81—H81···O81^{vi}	0.82(1)	2.44(1)	2.969(8)	123(2)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y+1, z$; (iii) $x, y+1, z$; (iv) $-x+2, -y+1, -z+1$; (v) $x-1, y, z$; (vi) $-x, -y+1, -z$.

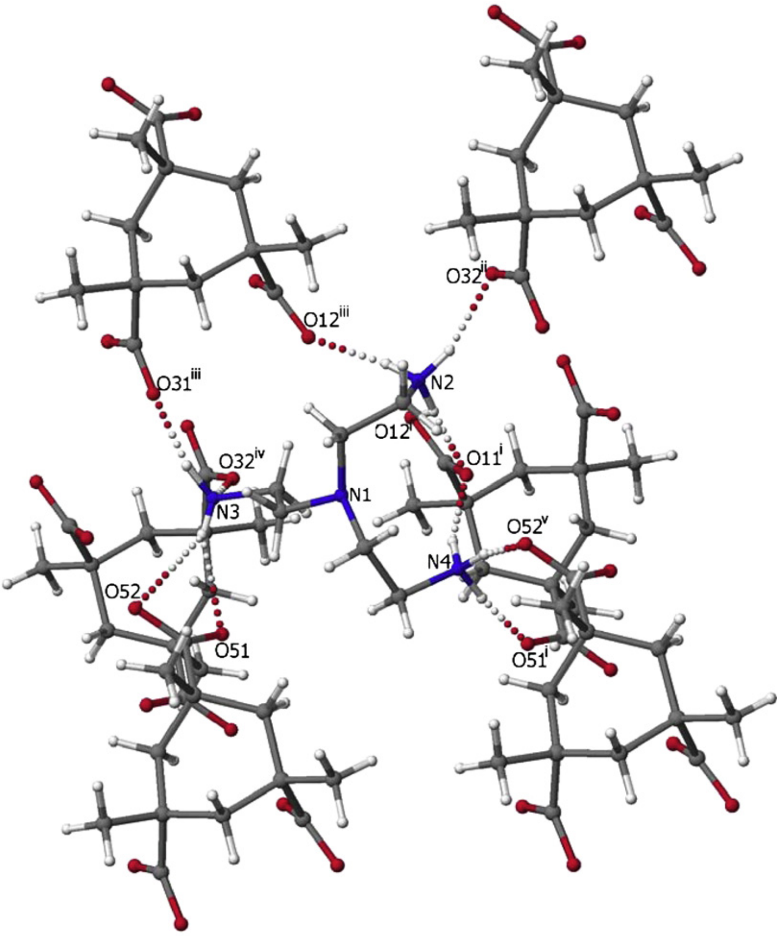

Fig. 2. Hydrogen-bonding environment of the H_3TAEA^{3+} cation. Symmetry code as in Table 3.

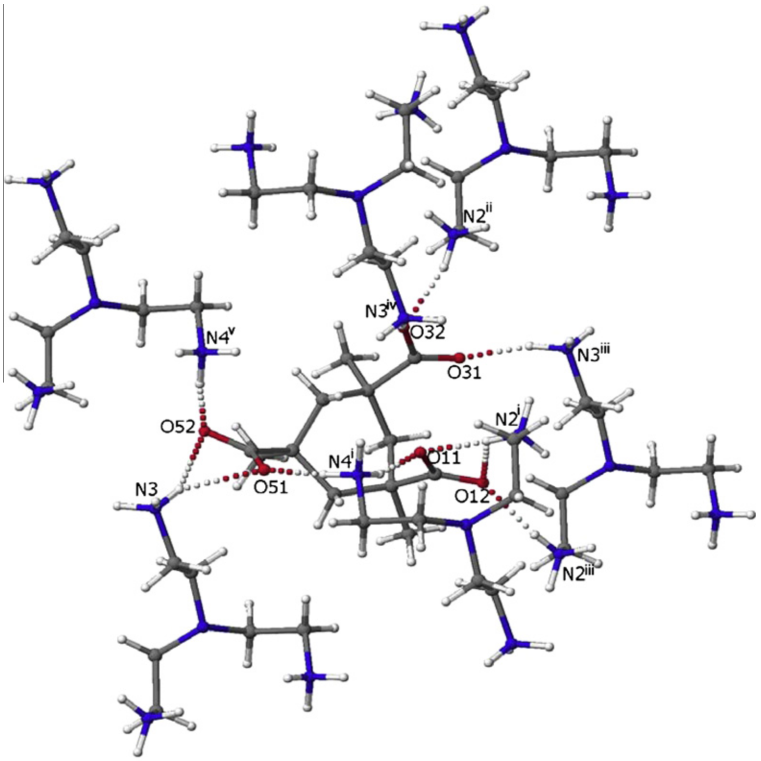

Fig. 3. Hydrogen-bonding environment of the KTA^{3-} trianion.

axial orientation of the COOH/COO$^-$ groups are retained after deprotonation (mono- or di). In all these structures, this conformation of H_2KTA^- and $HKTA^{2-}$ molecules is stabilised by the intramolecular charge-assisted O—H···O hydrogen bond [35,36]. In the present structure of H_3KTA–TAEA–EA the protons of the carboxyl groups of Kemps triacid are transferred to the nitrogen atoms of the amine groups of TAEA forming an H_3TAEA^{3+} cation (Fig. 1). After deprotonation the KTA^{3-} trianion with three carboxyalate groups (COO$^-$) change the conformation of the skeletal cyclohexane ring from chair to boat or twisted boat one as a result of mutual electrostatic repulsion between the COO$^-$ groups (Fig. S1, Suppl. mat.). The deprotonation of three carboxylic groups of Kemps triacid in the present structure is evidenced by the C—O bond lengths (Table 2), while the change in the conformation of the skeletal cyclohexane ring from chair to twisted boat is evidenced by the changes in the C—C—C—C torsion angles from ±60° as expected for the chair conformation (Table 2). The all six C—O bonds in the COO$^-$ groups are intermediate between the single $C(sp^2)$—O (1.308–1.320 Å) and double $C(sp^2)$=O (1.214–1.224 Å) [37] indicating delocalization of the charge onto both O atoms of the COO$^-$ groups. The H_3TAEA^{3+} cation exhibits distorted C_3 symmetry as expected for the isolated non-interacted cation. The C—N bonds linking the protonated amine groups are slightly longer than that involving the central N1 atom (Table 2). The values of the C—N bonds are in agreement with the expected values of $C(sp^3)$—NH_3^+ (1.482–1.495 Å) and the $C(sp^3)$—N (1.450–1.478 Å) [37] for the tertiary amines.

In the crystal, the arrangement of the oppositely charged units, KTA^{3-} and H_3TAEA^{3+}, is mainly determined by a combination of ionic and hydrogen bonding interactions and to a lesser degree by the van der Waals forces (Fig. S2, Suppl. mat.). Each KTA^{3-} trianion is surrounded by six triprotonated H_3TAEA^{3+} trications, so the KTA^{3-} trianion is an acceptor of eleven [COO$^-$···H_3N^+] hydrogen bonds (Table 3, Fig. 2). Each triprotonated H_3TAEA^{3+} cation is involved as a donor in the N—H···O hydrogen bonds with six neighbouring KTA^{3-} trianion (Fig. 3). The interacted and hydrogen-bonded {KTA^{3-}···H_3TAEA^{3+}} aggregates related by an inversion and translation along the *a* and *b* axes are arranged into layers parallel to the (0 0 1) crystallographic plane (Fig. S2, Suppl. mat.). The voids between the layers are occupied by the ethanol molecules, which interact with each other *via* O—H···O hydrogen bond forming a dimeric structure (Fig. S3, Suppl. mat.).

3.2. FT-IR studies

The FT-IR spectrum of the H_3KTA–TAEA–EA complex (solid line) is compared with the spectra of KTA (dashed line) and TAEA (dashed-dotted line) in Fig. 4a and the same spectra with extended scale in the regions of ν(OH) and ν(NH) as well as ν(C=O) vibrations in Fig. 4b and c, respectively. In the unit cell of the 1:1:1 H_3KTA–TAEA–EA crystal, each Kemp triacid molecule is completely deprotonated forming a trianion KTA^{3-}, which is hydrogen-bonded to the triprotonated H_3TAEA^{3+} trication *via* 11 intermolecular [COO$^-$···H_3N^+] hydrogen bonds (Figs. 2 and 3). The parameters of these hydrogen bonds are given in Table 3. These hydrogen bonds are rather weak or of intermediate strength and from the spectroscopic point of view, interpretation of the FT-IR spectrum of the hydrogen-bonded network in the crystal is difficult due to the overlapping of the respective $\nu(NH_3^+)$ stretching vibrations.

According to the crystal structure, two ethanol molecules are hydrogen-bonded, forming a dimer (Fig. S3, Suppl. mat.). However, these hydrogen bonds are very weak and therefore the band with a maximum at 3390 cm^{-1} should be assigned to the protonic vibration of a very weakly hydrogen-bonded OH group.

The bands assigned to the ν_{as}(N—H) and ν_s(N—H) vibrations at 3356 cm^{-1} and 3270 cm^{-1}, respectively and observed in the spectrum of TAEA (dash-dotted line) are no longer observed in the spectrum of 1:1:1 H_3KTA–TAEA–EA complex (solid line), which means that the three NH_2 amine groups of TAEA are protonated and hydrogen-bonded within the complex structure.

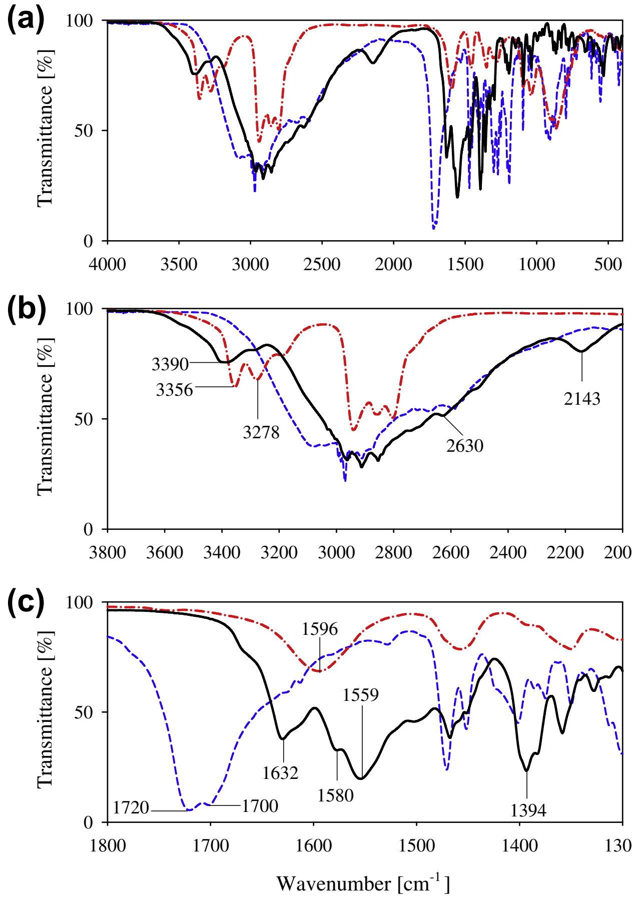

Fig. 4. FT-IR spectra in nujol/fluorolube mulls of: (- - -) H_3KTA, (– · –) TAEA and (—) H_3KTA–TAEA–EA complex in the ranges: (a) 4000–400 cm^{-1}; (b) 3800–2000 cm^{-1} and (c) 1800–1300 cm^{-1}.

The structure of Kemp's triacid (H_3KTA) is well known. The carboxylic groups of H_3KTA are hydrogen-bonded forming a dimeric carboxylic–carboxylic network in the crystal structure [29–31]. The vibrations of the protons within these hydrogen bonds are manifested as a broad structured band in the region 3400–2400 cm^{-1} (Fig. 4, dashed line). In contrast, the formation of [COO$^-$···H_3N^+] bonds is reflected in the spectrum of the complex as a broad absorption in the region from 3200 cm^{-1} to 2400 cm^{-1}.

In the spectrum of crystalline H_3KTA the appearance of two bands with the maxima at 1720 cm^{-1} and 1700 cm^{-1} (Fig. 4c, dashed line), connected with the ν(C=O) vibrations of the carboxylic groups, indicates that these groups are clearly different hydrogen-bonded within the structure of the hydrogen-bonded network. In the spectrum of the complex (solid line), these bands are no more observed and instead, a new band arises with a maximum at about 1559 cm^{-1} assigned to the ν_{as}(COO$^-$) vibrations. The respective band assigned to the ν_s(COO$^-$) vibrations is observed at 1394 cm^{-1}. Furthermore, the broad band at 1662 cm^{-1} is assigned to the $\delta(NH_3^+)$ vibrations of the protonated and hydrogen bonded TAEA molecule. The presence of these two bands connected with the respective ν_{as}(COO$^-$) and $\delta(NH_3^+)$ vibrations is the spectroscopic evidence of the complete proton transfer from the carboxylic groups of H_3KTA to the NH_2 groups of TEAA within the complex structure.

Appendix A. Supplementary material

The X-ray crystallographic data for the structure reported in this paper have been deposited at the CCDC as supplementary data, CCDC 816769. Copies of the data can be obtained on application to CCDC, 12 Union Road, Vambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.04.005.

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