
A. N. Chekhlov
Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia
Received November 5, 2006

Abstract—A crystalline hydrated salt of the 2.2.2-cryptand and phosphoric acid, \([H_2(Crypt-222)](HPO_4)^2- \cdot 8H_2O\) (I), is synthesized. Its crystal structure is studied using X-ray diffraction analysis (space group \(P2_1/\text{nm}\), \(a = 9.244\, \text{Å},\) \(b = 25.750\, \text{Å},\) \(c = 13.218\, \text{Å},\) \(\beta = 95.87^\circ,\) \(Z = 4\)); direct method, full-matrix least-squares method in the anisotropic approximation to \(R = 0.055\) for 4622 reflections, CAD4 automated diffractometer, \(\lambda\text{MoK}\alpha\) radiation). The structure contains the 2.2.2-cryptand dication with the rare \(exo-exo\) conformation with two \(\text{H}\) atoms at two \(\text{N}\) atoms directed outside from the cavity. A \(\text{P}\) atom of the \(\text{HPO}_4^{2-}\) anion has a considerably distorted tetrahedral coordination. The crystal of compound I contains a branched infinite three-dimensional system of intermolecular (interionic) hydrogen bonds.

DO: 10.1134/S0036023608040189

The 2.2.2-cryptand, being a diacidic base (tertiary diamine), forms salts with various acids. Continuing the study of crystal structures of its salts with inorganic acids, which is of certain interest for supramolecular chemistry [1], we synthesized a new salt with phosphoric acid: 4,7,13,16,21,24-hexaoxa-1,10-diaziabicyclo[8.8.8]hexacosane hydrogen phosphate octahydrate with the composition \([H_2(Crypt-222)](HPO_4)^2- \cdot 8H_2O\) (I), where \([H_2(Crypt-222)]^2+\) is the dication of the 2.2.2-cryptand\(^1\) with two protonated nitrogen atoms and studied its crystal structure by X-ray diffraction analysis.

Recently we synthesized and studied by X-ray diffraction analysis another crystalline salt of the 2.2.2-cryptand and phosphoric acid with the composition \([H_2(Crypt-222)]^2+ \cdot 2\text{HP}O_4^2- \cdot 2H_2O\) (II) [2].

EXPERIMENTAL

Synthesis of salt I. An aqueous solution of phosphoric acid \(\text{H}_3\text{PO}_4\) was added dropwise in the 1 : 1 (mol/mol) ratio to a solution of the 2.2.2-cryptand in ethanol. The mixture was left to evaporate at room temperature. After several days, colorless crystals of salt I precipitated on the bottom of the vessel.

X-ray diffraction analysis. The unit cell parameters and the three-dimensional set of reflection intensities were obtained on an Enraf-Nonius CAD4 X-ray automated diffractometer (MoK\(\alpha\) radiation, graphite monochromator). The crystals of salt I are monoclinic, \([\text{C}_{18}\text{H}_{38}\text{N}_8\text{O}_{16}]^{2+} \cdot \text{HPO}_4^{2-} \cdot 8\text{H}_2\text{O}\), FW = 618.61; \(a = 9.244(2)\, \text{Å},\) \(b = 25.750(4)\, \text{Å},\) \(c = 13.218(3)\, \text{Å},\) \(\beta = 95.87(2)^\circ,\) \(V = 3130(1)\, \text{Å}^3,\) \(Z = 4,\) \(\rho_{\text{calcld}} = 1.313\, \text{g/cm}^3,\) \(\mu(\text{MoK}\alpha) = 1.63\, \text{cm}^{-1},\) space group \(P2_1/\text{nm}\).

The intensities of 4979 reflections were measured in a quadrant of the reciprocal space \((2\theta \leq 47^\circ)\) in the 0/20 scan mode from a single crystal 0.20 \(\times\) 0.25 \(\times\) 1.25 mm in size. A special mode was used for measuring intensities, when the final scan was carried out for all reflections, including very weak ones. Absorption correction was applied to the reflection intensities by a semiempirical method [3]. After 136 pairs of systematically absent reflections were excluded and the intensities of 221 pairs of equivalent \(h\bar{k}0\) and \(\bar{h}k0\) reflections were averaged \(R_m = 0.021\), the working set of the measured \(F^2(hk\ell)\) and \(\sigma(F^2)\) values contained 4622 independent reflections.

The structure of salt I was solved by a direct method using the SHELXS97 program package [4] and refined by the full-matrix least-squares method for \(F^2\) using the SHELXL97 program package [4] in the anisotropic approximation for non-hydrogen atoms. Almost all reflections from the working set (including very weak reflections with \(I < 2\sigma(I)\)) were used in the refinement, except for several reflections with poorly consistent measured and calculated \(F^2\) values.

First, an ordered model for the structure of salt I was obtained by a direct method. During the further anisotropic refinement, the presence of appreciable \(\Delta p\) peaks...
in the difference Fourier synthesis and the values of the anisotropic thermal parameters $U_{ij}$ of the O atoms of some water molecules suggested that the O atoms of three of the eight independent water molecules are each disordered over two positions. The total site occupancies of the three pairs of these positions (along with other parameters) were refined introducing three additional varied parameters [4].

All independent H atoms in the 2.2.2-dication, the H atom of the HPO$_4^{2–}$ anion, and most of the H atoms of the eight water molecules, excluding some positions of the H atoms of the disordered water molecules, were objectively located in difference Fourier synthesis at an intermediate stage of the refinement of structure I.

Then, all positions of the H atoms of the 2.2.2-dication were specified geometrically: their coordinates were calculated by the riding model [4] in the refinement procedure for the structure of compound I, and individual isotropic thermal parameters $U_{iso}$ were refined for all of these H atoms. The coordinates and $U_{iso}$ of the H atom of the HPO$_4^{2–}$ anion were refined in the same manner as for the free atom.

The coordinates of the H atoms of all water molecules were refined imposing the mild geometric DFIX constraint [4] on short interatomic distances involving these atoms. Their $U_{iso}$ were not refined but fixed as having values 1.2–1.5 times the $U_{eq}$ of the corresponding water O atoms.

For an exposed crystal of salt I, the isotropic extinction coefficient was refined: $g = 0.011(1)$ [4]. In the last cycle of the full-matrix refinement, the absolute shifts of all the 465 variable parameters were less than 0.001σ.

The final coordinates and thermal parameters of the atoms are listed in Table 1.

The final refinement values are $R = 0.041$, $wR_2 = 0.105$ for 3650 observed reflections with $I \geq 2\sigma(I)$; $R = 0.055$, $wR_2 = 0.128$ for all independent reflections; the goodness-of-fit $S$ is 1.06 (the definition for $wR_2$ and $S$ is given in [4]). In the final difference Fourier synthesis, $-0.22 < \Delta \rho < 0.21$ e Å$^{-3}$. The used $f$-curves and anomalous dispersion corrections to them ($\Delta f'$ and $\Delta f''$) are borrowed from [5].

**RESULTS AND DISCUSSION**

The crystal structure of salt I contains symmetrically independent 2.2.2-dication, HPO$_4^{2–}$ anion, and eight water molecules, three of which are disordered. A fragment of the packing of crystal I is shown in Fig. 1, and the structure of the 2.2.2-dication is presented in Fig. 2. Bond lengths, bond angles, and selected torsion angles are listed in Table 2.

Then, all positions of the H atoms of the 2.2.2-dication were specified geometrically: their coordinates were calculated by the riding model [4] in the refinement procedure for the structure of compound I, and individual isotropic thermal parameters $U_{iso}$ were refined for all of these H atoms. The coordinates and $U_{iso}$ of the H atom of the HPO$_4^{2–}$ anion were refined in the same manner as for the free atom.

The coordinates of the H atoms of all water molecules were refined imposing the mild geometric DFIX constraint [4] on short interatomic distances involving these atoms. Their $U_{iso}$ were not refined but fixed as having values 1.2–1.5 times the $U_{eq}$ of the corresponding water O atoms.

For an exposed crystal of salt I, the isotropic extinction coefficient was refined: $g = 0.011(1)$ [4]. In the last cycle of the full-matrix refinement, the absolute shifts of all the 465 variable parameters were less than 0.001σ.

The final coordinates and thermal parameters of the atoms are listed in Table 1.

The final refinement values are $R = 0.041$, $wR_2 = 0.105$ for 3650 observed reflections with $I \geq 2\sigma(I)$; $R = 0.055$, $wR_2 = 0.128$ for all independent reflections; the goodness-of-fit $S$ is 1.06 (the definition for $wR_2$ and $S$ is given in [4]). In the final difference Fourier synthesis, $-0.22 < \Delta \rho < 0.21$ e Å$^{-3}$. The used $f$-curves and anomalous dispersion corrections to them ($\Delta f'$ and $\Delta f''$) are borrowed from [5].

**RESULTS AND DISCUSSION**

The crystal structure of salt I contains symmetrically independent 2.2.2-dication, HPO$_4^{2–}$ anion, and eight water molecules, three of which are disordered. A fragment of the packing of crystal I is shown in Fig. 1, and the structure of the 2.2.2-dication is presented in Fig. 2. Bond lengths, bond angles, and selected torsion angles are listed in Table 2.

**RESULTS AND DISCUSSION**

The crystal structure of salt I contains symmetrically independent 2.2.2-dication, HPO$_4^{2–}$ anion, and eight water molecules, three of which are disordered. A fragment of the packing of crystal I is shown in Fig. 1, and the structure of the 2.2.2-dication is presented in Fig. 2. Bond lengths, bond angles, and selected torsion angles are listed in Table 2.

**RESULTS AND DISCUSSION**

The crystal structure of salt I contains symmetrically independent 2.2.2-dication, HPO$_4^{2–}$ anion, and eight water molecules, three of which are disordered. A fragment of the packing of crystal I is shown in Fig. 1, and the structure of the 2.2.2-dication is presented in Fig. 2. Bond lengths, bond angles, and selected torsion angles are listed in Table 2.