



# Communication Diverse Hydrogen-Bonded Structural Motifs in 1,4-Diazabicyclo[2.2.2]octane N,N'-Dioxide Salts with Oxoanions

Ksenia D. Abasheeva <sup>1,2</sup>, Pavel A. Demakov <sup>1,\*</sup> and Vladimir P. Fedin <sup>1</sup>

- <sup>1</sup> Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Akad. Lavrenteva Ave., 630090 Novosibirsk, Russia
- <sup>2</sup> Department of Natural Sciences, Novosibirsk State University, 2 Pirogova St., 630090 Novosibirsk, Russia
- \* Correspondence: demakov@niic.nsc.ru; Tel.: +7-(383)-330-9489

**Abstract:** Four new hybrid inorganic–organic salts of 1,4-diazabicyclo[2.2.2]octane N,N'-dioxide (odabco) with the formulae odabco·2HNO<sub>3</sub> (1), odabco·HClO<sub>4</sub> (2), odabco·H<sub>2</sub>SO<sub>4</sub> (3) and odabco·2H<sub>2</sub>SO<sub>4</sub> (4) were synthesized and characterized by single-crystal x-ray diffraction (XRD), powder XRD and infrared spectroscopy. Compound **1** is based on the isolated (H<sub>2</sub>odabco)<sup>2+</sup> fragments, representing 0D structure. **2** is based on cationic 1D {Hodabco}<sub>n</sub><sup>n+</sup> hydrogen-bonded chains. Compound **3** comprising a strongly coordinated sulfate anion consists of two-component hydrogen-bonded {-H<sub>2</sub>odabco-SO<sub>4</sub>\_} fragments forming uncharged 1D helical chains. **4** contains both {-HSO<sub>4</sub>-}<sub>n</sub><sup>n-</sup> and {-HSO<sub>4</sub>-H<sub>2</sub>odabco-HSO<sub>4</sub>\_} hydrogen bonding motifs, resulting in a 3D polymeric network. A comparative structural analysis of both the obtained and the previously reported cognate structures was performed to rationalize the impact of the degree of odabco protonation and the anion donor ability on the structural features and dimensionalities of odabco-based hydrogen-bonded lattices.

**Keywords:** hydrogen bond; salts; HOFs; dabco N,N'-dioxide; nitrate; perchlorate; sulfate; crystal structure

## 1. Introduction

1,4-diazabicyclo[2.2.2]octane N,N'-dioxide (odabco) moiety contains quite sterically unhindered oxygen atoms with a high donor ability (Scheme 1a) [1–4]. Therefore, odabco can easily act as both a ligand in metal complexes [5–8] and a protonated cation in salts with inorganic [9–11] or organic anions [12,13]. Diverse types of such alicyclic moiety mobility (Scheme 1b-d) provide structural phase transitions in odabco-based compounds; hence, they can precede their functional properties, e.g., piezo-, para- and ferroelectricity [10,12,14]. In addition, low UV/vis absorption of the saturated odabco molecule is a valuable feature in the design of optical metal–organic framework materials [15]. Thus, the synthesis and acquisition of a structural library of new odabco-based compounds are of great interest for their possible applications as ligand sources and paraelectric-type materials. This work reports the preparation, crystal structures and characterization of four new protonated 1,4-diazabicyclo[2.2.2]octane N,N'-dioxide salts containing oxoanions of readily available nitric, sulfuric and perchloric acids, namely, odabco·2HNO<sub>3</sub> (1), odabco· $HClO_4$  (2), odabco· $H_2SO_4$  (3) and odabco· $2H_2SO_4$  (4). A comprehensive structural analysis of the obtained virtual library, appended by the previously reported structures odabco·HNO<sub>3</sub> [16] and odabco·2HClO<sub>4</sub>·2H<sub>2</sub>O [10], was performed. Depending on both the degree of odabco protonation and the donor strength of the anions, the presented salts form structures of diverse dimensionalities and modes of hydrogen bonding.



Citation: Abasheeva, K.D.; Demakov, P.A.; Fedin, V.P. Diverse Hydrogen-Bonded Structural Motifs in 1,4-Diazabicyclo[2.2.2]octane N,N'-Dioxide Salts with Oxoanions. *Molbank* 2022, 2022, M1508. https://doi.org/10.3390/M1508

Academic Editor: Kristof Van Hecke

Received: 3 November 2022 Accepted: 23 November 2022 Published: 25 November 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).



**Scheme 1.** Charge-separated structural formula of 1,4-diazabicyclo[2.2.2]octane N,N'-dioxide (odabco) (**a**). Highly fluidic enantiomeric forms (**b**), axial rotation mode (**c**) and torsion mode (**d**) of odabco.

## 2. Results and Discussion

#### 2.1. Crystal Structures

Compound odabco·2HNO<sub>3</sub> (1) crystallizes in monoclinic symmetry with the  $P2_1/n$  space group. The asymmetric unit of 1 consists of one twice-protonated odabco cation and two nitrate anions. Both nitrates are hydrogen-bound as donors to  $(H_2odabco)^{2+}$  acceptor moiety with the corresponding  $O(NO_3)...O(odabco)$  distances of 2.55 and 2.56 Å (Figure 1a). Weak  $\pi-\pi$  stacking interactions between the neighboring nitrates are notable, with 3.27 Å as the closest intermolecular N...O distance and 3.24 Å interplanar distance. The closest  $O(NO_3)...C(odabco)$  distance is 3.22 Å, representing no strong interactions between the nitrate and odabco aliphatic core. Furthermore, no significant contact appears between the closest organic cations due to the chess-like packing of  $(H_2odabco)^{2+}$  and  $(NO_3^-)_2$  pairs in 1's crystal structure (Figure 1b). Therefore, in terms of the hydrogen bonding system, 1 can be considered as a zero-dimensional structure.



**Figure 1.** Two neighboring odabco-2HNO<sub>3</sub> fragments in **1**. Hydrogen bonds are shown dashed orange (**a**). View of crystal packing along *a* axis in **1** (**b**).

The comparison of **1** to the previously reported structure odabco·HNO<sub>3</sub> [16] reveals different types of strong intermolecular interactions. In odabco·HNO<sub>3</sub>, a monoprotonated organic cation forms slightly entangled one-dimensional polymeric chains {-Hodabco-}<sub>n</sub><sup>n+</sup>, in which neighboring monomeric moieties are bound to each other through hydrogen bonds with 2.44 Å O(odabco)...O(odabco) intermolecular distances. A nitrate anion appears not to be included into the system of hydrogen bonds. Such a principal difference between the structures of mono- and diprotonated odabco nitrates can be explained by the higher donor strength of odabco oxygen compared to the nitrate, illustrating a presence of a high negative charge on the odabco oxygen (see Scheme 1a).

The odabco·HClO<sub>4</sub> compound (2) crystallizes in monoclinic symmetry with the  $P2_1/n$  space group. The asymmetric unit consists of one monoprotonated odabco cation and one perchlorate anion. The organic moieties of **2** are hydrogen-bonded one to another in a similar way to the abovementioned odabco·HNO<sub>3</sub> [16] manner by strong hydrogen bonds forming 1D chains (Figure 2a) with the corresponding O(odabco)...O(odabco) intermolecular distances of 2.45 Å. The perchlorate anion is, in the same way, not included in the system of hydrogen bonds, only weakly contacting to the odabco aliphatic core (Figure 2b) with the shortest C(odabco)...O(ClO<sub>4</sub>) distance of 2.93 Å. The torsion angles H-O-O-H within {-Hodabco-}<sub>n</sub><sup>n+</sup> polymeric chains are 136° in odabco·HNO<sub>3</sub> and 144° odabco·HClO<sub>4</sub> (**2**, see Figure 2a), respectively, showing an almost anion-independent similarity of the chain geometry and entanglement.



**Figure 2.** {-Hodabco-} $_n^{n+}$  chains and ClO<sub>4</sub><sup>-</sup> counter anions in the structure of **2**. Hydrogen bonds are shown dashed orange (**a**). View of crystal packing along [-1 0 -1] special axis in **2** (**b**).

An analysis of the previously reported structure of bis-perchlorate odabco·2HClO<sub>4</sub>· 2H<sub>2</sub>O [10] was also carried out for full representativity. This compound is based on the twice-protonated odabco cations, which are hydrogen-bonded as acceptors to water donor molecules. The corresponding O(odabco)...O(H<sub>2</sub>O) distances are 2.57 Å, indicating the presence of a relatively strong hydrogen bond. Perchlorate anions are connected only as the donors with the water acceptor through weak hydrogen contacts, with O(H<sub>2</sub>O)...O(ClO<sub>4</sub>) distances of 2.96 Å and 2.97 Å, showing the much poorer binding energy of the perchlorate anion compared to the water, again consistent to the low donor ability of this anion. No polymeric system of hydrogen bonds appears in odabco·2HClO<sub>4</sub>·2H<sub>2</sub>O. Therefore, in terms of the hydrogen bonding system, this structure is zero-dimensional, similarly to 1, besides the presence of water in the crystal structure of odabco·2HClO<sub>4</sub>·2H<sub>2</sub>O. In summary, poorly coordinating nitrate and perchlorate adopt quite a similar structure-forming behavior in the discussed odabco salts.

The odabco·H<sub>2</sub>SO<sub>4</sub> compound (**3**) crystallizes in orthorhombic symmetry with the *Pnna* space group. The asymmetric unit consists of two independent halves of the odabco cation, both of which are protonated, and one sulfate anion. Sulfate is hydrogen-bound as a donor to the (H<sub>2</sub>odabco)<sup>2+</sup> acceptor with the corresponding O(SO<sub>4</sub>)...O(odabco) distances of 2.48 and 2.50 Å. These cationic and anionic moieties alternate within one-dimensional chains (Figure 3a). The behaviour of SO<sub>4</sub><sup>2-</sup> thereby drastically differs to the behaviour of nitrate and perchlorate described above, because, unlike those anions, sulfate is both a relatively strong donor and a possible bridge in the formation of hydrogen bonds. This feature results in the two-component hydrogen-bonded polymeric network. The described chains are twisted into helices around 2<sub>1</sub> screw axes (Figure 3b), which is apparently provided by the presence of low (ca. 53.2°) H-O-O-H torsion angles in the H<sub>2</sub>odabco<sup>2+</sup> cation along with the tetrahedral geometry (ca. 109.5° valence angle) of the sulfate anion. The chains are packed in a crystal structure without any strong interchain interactions,

as the strongest intermolecular contact between the chains is represented by a 2.99 Å  $C(odabco)...O(SO_4)$  distance. Therefore, in terms of the hydrogen bonding system, **3** is a one-dimensional polymeric structure. Unlike the above-described 1D salts, odabco·HNO<sub>3</sub> and odabco·HClO<sub>4</sub>, both comprising cationic {-Hodabco-}<sub>n</sub><sup>n+</sup> polymeric chains, **3** is based on uncharged {-H<sub>2</sub>odabco-SO<sub>4</sub>-}<sub>n</sub> chains, thus having no additional counteranion in its crystal structure. Such a difference between **3** and the corresponding mononitrate and monoperchlorate is apparently attributed to the high donor ability of the sulfate anion, when compared to nitrate and perchlorate anions, making it able to be incorporated into the polymeric hydrogen bond system.



**Figure 3.**  $\{-H_2 \text{odabco-SO}_4-\}_n$  chains in the structure of **3**. Hydrogen bonds are shown dashed orange (**a**). Schematic illustration of crystal packing along *b* axis in **3**. Independent chains are shown in different colors. S atoms and odabco centroids are shown as nodes (**b**).

The odabco- $2H_2SO_4$  compound (4) crystallizes in monoclinic symmetry with the *Cc* space group. The asymmetric unit consists of one twice-protonated odabco cation and two monoprotonated sulfates. Each hydrosulfate anion is interlinked through hydrogen bonds, both with two neighbouring HSO<sub>4</sub><sup>-</sup> and one (H<sub>2</sub>odabco)<sup>2+</sup>, resulting in a complicated system of hydrogen bonds (Figure 4a). The O(SO<sub>4</sub>)...O(SO<sub>4</sub>) distances between hydrogen-bonded hydrosulfates are 2.53 and 2.58 Å. The O(SO<sub>4</sub>)...O(odabco) distances to the hydrogen-bonded odabco cations are 2.55 and 2.60 Å, allowing us to speculate that slightly more strongly bound {-HSO<sub>4</sub>-}<sub>n</sub><sup>n-</sup> chains act as the main structural motif in **4**. These 1D chains lying in two almost perpendicular directions are interlinked by the hydrogen-bonded organic cation (Figure 4b), which acts thereby as a bridge between the poly-hydrosulfate chains. The resulting polymeric structure therefore appears to be the three-dimensional framework, again uncharged, similarly to the monosulfate **3** described above.



**Figure 4.** Two perpendicular  $\{-HSO_4-\}_n^{n-}$  chains interconnected by a  $(H_2odabco)^{2+}$  linker in the structure of **4**. Only one asymmetric unit is shown with 0% transparency (**a**). Schematic illustration of crystal packing along *c* axis in **4**. Independent chains are shown in different colors. S atoms are shown as nodes; odabco linkers are shown as orange dashed lines (**b**).

### 2.2. Characterization

All the salts were successfully prepared by the reaction of readily available odabco- $3H_2O_2$  [1,8] with acids in different solvents. PXRD patterns of the synthesized samples 1–4 (Figures S1–S4) correspond well to the theoretical ones, taking into account some reasonable shifting of the diffraction peaks to lower angles due to performing SCXRD at low temperatures and the subsequent thermal expansion of the crystal lattices at room temperature, at which the PXRD data were obtained. The infrared spectrum of 1 (Figure S5) contains a very strong band at 1381  $\text{cm}^{-1}$ , corresponding to the N-O valence vibration in the nitrate anion. The IR spectrum of 2 (Figure S6) contains a very strong band at 1096  $cm^{-1}$  and a strong band at 624 cm<sup>-1</sup>, corresponding to Cl-O valence vibrations in the perchlorate anion. The infrared spectrum of 3 (Figure S7) contains a strong band at 1120 cm<sup>-1</sup> and a medium band at 620 cm<sup>-1</sup>, corresponding to S-O valence stretchings in the sulfate anion. In 4, the corresponding bands are shifted down to  $1073 \text{ cm}^{-1}$  and  $576 \text{ cm}^{-1}$ , respectively (see Figure S7), due to the protonation of the sulfate anion [17]. Very weak C(sp<sup>3</sup>)-H vibration bands of the odabco aliphatic core appear in the 2820–2930 cm<sup>-1</sup> region, accordingly to the previously published results [8,15]. Medium (1, 2) and weak (3, 4) split bands in the 3000–3050 cm<sup>-1</sup> region indicate an involvement of protonated odabco moieties in hydrogen bonding [12]. The IR spectrum of 4 also contains a medium band at 1284 cm<sup>-1</sup>, which is absent in the spectrum of **3**, indicating a presence of SOH plane bending oscillations [17] in the hydrosulfate-containing 4.

## 3. Materials and Methods

ATTENTION: care should be taken in all the procedures carried out with 1,4-diazabicyclo octane N,N'-dioxide tris-(hydrogen peroxide) solvate (odabco $\cdot$ 3H<sub>2</sub>O<sub>2</sub>) and odabco compounds with potentially explosive anions, such as nitrate and perchlorate.

#### 3.1. Materials

Nitric acid (62% wt.) water solution, perchloric acid (65% wt.) water solution, sulfuric acid (98% wt.) and DMF (high purity grade) were commercially available and used as received. odabco $\cdot 3H_2O_2$  was synthesized according to the previously published procedure [8]. Distilled water was used in all the experiments.

#### 3.2. Instruments

Infrared (IR) spectra were obtained in the 4000-400 cm<sup>-1</sup> range using a Bruker Scimitar FTS 2000 spectrometer in KBr pellets. Elemental CHNS analyses were carried out using a VarioMICROcube device. Powder X-ray diffraction (PXRD) data were acquired with a Shimadzu XRD-7000 diffractometer (Cu-K $\alpha$  radiation,  $\lambda = 1.54178$  Å) at room temperature. <sup>1</sup>H NMR spectra were recorded on a Bruker Advance 500 NMR spectrometer (500.13 Hz). The analyte solutions for NMR were prepared by dissolving ca. 5 mg of each salt in 0.8 mL of  $D_2O$ . Diffraction data for single crystals of 1–4 were collected with an automated Agilent Xcalibur diffractometer equipped with an AtlasS2 area detector and graphite monochromator ( $\lambda$ (MoK $\alpha$ ) = 0.71073 Å). The CrysAlisPro program package [18] was used for the integration, absorption correction and determination of unit cell parameters. The dual space algorithm (SHELXT [19]) was used for the structure solution and the full-matrix least-squares technique (SHELXL [20]) was used for structure refinement. Anisotropic approximation was applied for all atoms, except hydrogens. Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. Details for single-crystal structure determination experiments and structure refinements are summarized in Appendix A, Table A1. CCDC 2205241 (1), 2205243 (2), 2205239 (3), 2205240 (4) entries contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at https://www.ccdc.cam.ac.uk/structures/.

## 3.3. Synthesis of Odabco · 2HNO<sub>3</sub> (1)

In an evaporating cup, odabco· $3H_2O_2$  (218 mg, 0.89 mmol),  $H_2O$  (5.0 mL) and HNO<sub>3</sub> (126 µL) were mixed. The evaporating cup with the solution was left at room temperature until the water completely evaporated, then the precipitated crystals were recrystallized from a minimal amount of water. The resulting colorless needles of **1** were filtered off and dried in air. The yield was 226 mg (95%). IR,  $\nu/cm^{-1}$ : 3422 (s), 3373 (w), 3074 (w), 3054 (w), 3026 (m), 3017 (m), 2974 (w), 2880 (w), 2856 (w), 2834 (w), 2794 (w), 2726 (m), 2700 (m), 2633 (w), 2592 (w), 2549 (w), 2498 (w), 2424 (w), 2301 (w), 1997 (w), 1764 (w), 1625 (m), 1557 (w), 1534 (m), 1498 (m), 1444 (w), 1427 (m), 1384 (s), 1275 (s), 1183 (w), 1104 (m), 1033 (s), 917 (m), 849 (s), 823 (w), 719 (w), 656 (m), 472 (m). Elemental analysis (%): Found C, 26.7; H, 5.1; N, 20.4, calculated for odabco·2HNO<sub>3</sub> (C<sub>6</sub>H<sub>14</sub>O<sub>8</sub>N<sub>4</sub>): C, 26.7; H, 5.2; N, 20.7. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): 4.154 (s).

## 3.4. Synthesis of Odabco $\cdot$ HClO<sub>4</sub> (2)

In an evaporating cup, odabco· $3H_2O_2$  (218 mg, 0.89 mmol),  $H_2O$  (5.0 mL) and HClO<sub>4</sub> (82 µL) were mixed. The evaporating cup with the solution was left at room temperature until the water completely evaporated, then the precipitated crystals were recrystallized from a minimal amount of water. The resulting colorless crystals of **2** were filtered off and dried in air. The yield was 203 mg (94%). IR,  $\nu/cm^{-1}$ : 3433 (s), 3045 (s), 3016 (w), 3006 (m), 2971 (w), 2912 (w), 2025 (m), 1640 (m), 1476 (m), 1376 (w), 1358 (w), 1144 (w), 1095 (m), 1042 (w), 1004 (w), 957 (w), 868 (m), 855 (m), 726 (s), 670 (s), 623 (s), 551 (s), 525 (m), 476 (m), 450 (s). No elemental CHNCl analysis was performed due to the high explosion hazard of the organic perchlorates. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): 4.309 (s).

## 3.5. Synthesis of $Odabco \cdot H_2SO_4$ (3)

In a glass vessel with a screw cap, odabco· $3H_2O_2$  (218 mg, 0.89 mmol), DMF (5.0 mL) and  $H_2SO_4$  (75 µL) were mixed. The mixture was treated in an ultrasonic bath for 10 min and kept at 100°C for 3 h. The resulting precipitate was filtered on a porous paper filter, washed with DMF, and dried in air to obtain colorless crystals of **3**. The yield was 191 mg (91%). IR,  $\nu/cm^{-1}$ : 3433 (m), 2049 (w), 3026 (w), 2980 (w), 2779 (w), 1718 (w), 1588 (w), 1470 (w), 1352 (w), 1119 (s), 939 (s), 855 (m), 621 (m), 592 (m), 483 (m). Elemental analysis (%): Found C, 28.2; H, 6.1; N, 11.4; S, 15.0, calculated for odabco· $H_2SO_4$ ·(Me<sub>2</sub>NH<sub>2</sub>HSO<sub>4</sub>)<sub>0.3</sub> (C<sub>6.6</sub>H<sub>16.7</sub>O<sub>7.2</sub>N<sub>2.3</sub>S<sub>1.3</sub>): C, 27.8; H, 5.9; N, 11.3; S, 14.6. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): 4.205 (s).

## 3.6. Synthesis of Odabco $\cdot 2H_2SO_4$ (4)

In an evaporating cup, odabco· $3H_2O_2$  (218 mg, 0.89 mmol),  $H_2O$  (5.0 mL) and  $H_2SO_4$  (100 µL) were mixed. The evaporating cup with the solution was left at room temperature until the water completely evaporated, then the precipitated crystals were recrystallized from a minimal amount of water. The resulting colorless crystals of 4 were filtered off and dried in air. The yield was 258 mg (86%). IR,  $\nu/cm^{-1}$ : 3435 (m), 3354 (m), 3033 (w), 3015 (w), 2996 (w), 2862 (w), 2822 (w), 2796 (w), 2746 (w), 2686 (w), 2612 (w), 2524 (w), 2466 (w), 1996 (w), 1746 (w), 1636 (w), 1593 (w), 1507 (s), 1470 (w), 1458 (m), 1451 (m), 1376 (w), 1334 (m), 1284 (m), 1181 (m), 1107 (w), 1069 (s), 1042 (w), 1007 (s), 887 (m), 850 (m), 652 (m), 613 (m), 578 (m), 456 (s). Elemental analysis (%): Found C, 21.4; H, 4.6; N, 8.2; S, 19.0, calculated for odabco· $2H_2SO_4(C_6H_{16}O_{10}N_2S_2)$ : C, 21.2; H, 4.7; N, 8.2; S, 18.9. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm): 4.280 (s).

## 4. Conclusions

To summarize, four new salts of 1,4-diazabicyclo[2.2.2]octane N,N'-dioxide (odabco) with different anions were synthesized and structurally characterized. A comparative analysis of the structural features for the new salts and two previously reported cognate structures was performed, revealing hydrogen bonding as a main structure-driving factor. Both the chemical nature and dimensionality of forming hydrogen bond networks were found to be anion-dependent. Perchlorate bearing the weakest donor ability among the

applied anions is not included in strong hydrogen bonds in its odabco salts, which results in the low dimensionality (0D or 1D) of the forming structures. Nitrate, being a bit stronger than perchlorate, but still a weak donor, may be involved in hydrogen bonding to protonated odabco cations, with no remarkable changes in the general structural motifs and dimensionality of the lattices. Sulfate, bearing the strongest donor ability among the considered anions, is involved in hydrogen bond systems in a bridging manner, which results in an increase in the polymeric lattice dimensionality to 1D or 3D. The reported results contribute to the further structural design of odabco-based optical and paraelectric materials.

**Supplementary Materials:** Figure S1: Experimental PXRD pattern of **1** sample compared to the theoretical one; Figure S2: Experimental PXRD pattern of **2** sample compared to the theoretical one; Figure S3: Experimental PXRD pattern of **3** sample compared to the theoretical one; Figure S4: Experimental PXRD pattern of **4** sample compared to the theoretical one; Figure S5: Infrared spectrum of **1**; Figure S6: Infrared spectrum of **2**; Figure S7: Infrared spectra of **3** and **4**; Figure S8: <sup>1</sup>H NMR spectra for **1** (a), **2** (b), **3** (c) and **4** (d) in D<sub>2</sub>O. Peaks at ~4.71 ppm correspond to the residual mobile <sup>1</sup>H protons in D<sub>2</sub>O.

**Author Contributions:** K.D.A.—writing (original draft preparation), synthesis, characterization, visualization. P.A.D.—writing (original draft preparation), single-crystal XRD, visualization, conceptualization, project administration, funding acquisition. V.P.F.—writing (manuscript review and editing), resources. All authors have read and agreed to the published version of the manuscript.

**Funding:** The research was supported by the Russian Science Foundation, project № 22-23-20179, https://rscf.ru/project/22-23-20179/, and the Government of Novosibirsk region, project № p-22.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Samples of compounds 1–4 are available from the authors.

Acknowledgments: The authors thank Sergey S. Patrushev (NSU) for helpful discussions and XRD facilities of NIIC SB RAS and personally thank Ilya V. Korol'kov for the PXRD data collection.

Conflicts of Interest: The authors declare no conflict of interest.

#### Appendix A. Crystallographic Data

Table A1. The crystallographic data and structure refinement details for 1–4.

	1	2	3	4
Chemical formula	$C_6H_{14}N_4O_8$	$C_6H_{13}ClN_2O_6$	$C_6H_{14}N_2O_6S$	$C_{6}H_{16}N_{2}O_{10}S_{2}$
M <sub>r</sub> , g/mol	270.21	244.63	242.25	340.33
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_{1}/n$	Pnna	Сс
Temperature, K	150	150	135	150
<i>a</i> , Å	6.6537(4)	7.8923(4)	11.6565(7)	9.5987(3)
b, Å	18.9836(11)	11.6883(4)	23.8750(14)	10.3468(3)
<i>c,</i> Å	8.5758(5)	10.6752(4)	7.0514(4)	12.7952(5)
α, °	90	90	90	90
b, °	94.448(6)	98.338(4)	90	102.635(4)
γ, °	90	90	90	90
<i>V</i> , Å <sup>3</sup>	1079.96(11)	974.35(7)	1962.4(2)	1239.99(7)
$D(\text{calc.}), \text{g}\cdot\text{cm}^{-3}$	1.662	1.668	1.640	1.823

	1	2	3	4
μ, mm <sup>-1</sup>	0.15	0.41	0.34	0.49
Crystal size, mm	$0.53\times0.30\times0.29$	$0.70\times0.60\times0.34$	$0.68\times0.26\times0.15$	$0.53 \times 0.35 \times 0.26$
$\theta$ range for data collection, °	$2.2 < \theta < 25.3$	$2.6 < \theta < 25.4$	$3.4 < \theta < 25.4$	$2.9 < \theta < 25.4$
No. of reflections: mea- sured/independent/observed $[I > 2\sigma(I)]$	8569/ 1974/ 1730	6851/ 1783/ 1622	5377/ 1796/ 1564	9464/ 2296/ 2258
R <sub>int</sub>	0.0213	0.0222	0.0168	0.0201
Index ranges	$-7 \le h \le 8$ $-22 \le k \le 22$ $-10 \le l \le 18$	$-9 \le h \le 6$ $-14 \le k \le 14$ $-12 \le l \le 12$	$-12 \le h \le 14$ $-20 \le k \le 28$ $-8 \le l \le 6$	$-11 \le h \le 11$ $-12 \le k \le 12$ $-15 \le l < 15$
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0327$ $wR_2 = 0.0818$	$R_1 = 0.0308$ $wR_2 = 0.0845$	$R_1 = 0.0314$ $wR_2 = 0.0792$	$R_1 = 0.0218$ $wR_2 = 0.0558$
Final <i>R</i> indices (all data)	$R_1 = 0.0388$ $wR_2 = 0.0853$	$R_1 = 0.0343$ $wR_2 = 0.0866$	$R_1 = 0.0381$ $wR_2 = 0.0824$	$R_1 = 0.0222 \\ wR_2 = 0.0562$
Goodness of fit on $F^2$	1.073	1.068	1.060	1.098
Largest diff. peak, hole, $e/Å^3$	0.22, -0.26	0.26, -0.39	0.28, -0.41	0.16, -0.31

#### Table A1. Cont.

#### References

- 1. Hon, P.K.; Mak, T.C.W. Isolation and crystal structures of 1:3 molecular complexes of triethylenediamineN,N'-dioxide with hydrogen peroxide and water. *J. Crystallogr. Spectrosc. Res.* **1987**, *17*, 419–429. [CrossRef]
- Harmon, K.M.; Akin, A.C. Hydrogen bonding Part 40. IR and thermodynamic study of stability and stoichiometry for triethylenediamine dioxide hydrates, triethylenediamine monohydrate, and a mixed H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub> solvate of triethylenediamine dioxide. *J. Mol. Struct.* 1992, 265, 59–73. [CrossRef]
- 3. Medvedev, A.G.; Churakov, A.V.; Prikhodchenko, P.V.; Lev, O.; Vener, M.V. Crystalline Peroxosolvates: Nature of the Coformer, Hydrogen-Bonded Networks and Clusters, Intermolecular Interactions. *Molecules* **2021**, *26*, 26. [CrossRef] [PubMed]
- 4. Saraswatula, V.G.; Bhat, M.A.; Gurunathana, P.K.; Saha, B.K. Comparison of pyridyl and pyridyl N-oxide groups as acceptor in hydrogen bonding with carboxylic acid. *CrystEngComm* **2014**, *16*, 4715–4721. [CrossRef]
- 5. Sun, F.-X.; Zhu, G.-S.; Fang, Q.-R.; Qiu, S.-L. A novel 3D metal-organic framework with the pcu topology constructed from 1,4-diaza-bicyclo[2.2.2]octane-N,N'-dioxide. *Inorg. Chem. Comm.* 2007, 10, 649. [CrossRef]
- Abasheeva, K.D.; Demakov, P.A.; Dybtsev, D.N.; Fedin, V.P. Crystal Structure of Coordination cobalt(II) and zinc(II) Polymers with 1,4-diazabicyclo[2.2.2]octane N,N'-dioxide. J. Struct. Chem. 2022, 63, 1349–1357. [CrossRef]
- Zheng, B.; Luo, J.; Wang, F.; Peng, Y.; Li, G.; Huo, Q.; Liu, Y. Construction of Six Coordination Polymers Based on a 5,5'-(1,2-Ethynyl)bis-1,3-benzenedicarboxylic Ligand: Synthesis, Structure, Gas Sorption, and Magnetic Properties. *Cryst. Growth Des.* 2013, 13, 1033–1044. [CrossRef]
- Demakov, P.A.; Romanov, A.S.; Samsonenko, D.G.; Dybtsev, D.N.; Fedin, V.P. Synthesis and structure of manganese(II) coordination polymers with 1,4-diazabicyclo[2.2.2]octane N, N'-dioxide: Solvent and template effects. *Russ. Chem. Bull.* 2020, 69, 1511–1519. [CrossRef]
- Liao, W.-Q.; Zhou, Q.-Q.; Zhang, Y. catena-Poly[1,4-dihy droxy-1,4-di azoniabicyclo [2.2.2]octane[aqua tri-[mu]-chloridotrichloridodicuprate(II)]]. Acta Crystallogr. 2013, C69, 380–383. [CrossRef]
- 10. Chen, L.Z.; Sun, J. Reversible ferroelectric phase transition of 1,4-diazabicyclo[2,2,2]octane N,N'-dioxide di(perchlorate). *Inorg. Chem. Comm.* **2017**, *76*, 67–70. [CrossRef]
- 11. Leblanc, N.; Allain, M.; Mercier, N.; Cariati, E. Protonated *N*,*N*'-Dioxide-4,4'-bipyridine, an Interesting Synthon for the Building of Polar H-Bonded Networks? *Cryst. Growth Des.* **2011**, *11*, 5200–5205. [CrossRef]
- 12. Ye, H.-Y.; Zhang, Y.; Noro, S.-I.; Kubo, K.; Yoshitake, M.; Liu, Z.-Q.; Cai, H.-L.; Fu, D.-W.; Yoshikawa, H.; Awaga, K.; et al. Molecule-displacive ferroelectricity in organic supramolecular solids. *Sci. Rep.* **2013**, *3*, 2249. [CrossRef] [PubMed]
- 13. Sandipan Roy, S.; Biradha, K. Exploration of Salts and Cocrystals of 2,2',6,6'-Tetracarboxybiphenyl with Acetic Acid, Monobasic and Dibasic N-Heterocycles, and N-Oxides. *Cryst. Growth Des.* **2013**, *13*, 3232–3241. [CrossRef]
- Chen, L.; Ji, Q.; Wang, X.; Pan, Q.; Cao, X.; Xu, G. Two novel metal–organic coordination polymers based on ligand 1,4diazabicyclo[2.2.2]octane N,N'-dioxide with phase transition, and ferroelectric and dielectric properties. *CrystEngComm* 2017, 19, 5907–5914. [CrossRef]

- Demakov, P.A.; Samsonenko, D.G.; Dybtsev, D.N.; Fedin, V.P. Zinc(II) metal-organic frameworks with 1,4-diazabicyclo[2.2.2]octane N,N'-dioxide: Control of the parameters of the cationic porous framework and optical properties. *Russ. Chem. Bull.* 2022, 71, 83–90. [CrossRef]
- Demakov, P.A.; Yudina, Y.A.; Samsonenko, D.G.; Dybtsev, D.N.; Fedin, V.P. Crystal structure of zinc coordination polymers based on 1,4-diazabicyclo[2.2.2]octane N,N'-dioxide: Effect of hydrophobicity of carboxylate ligands. J. Struct. Chem. 2021, 62, 403–411. [CrossRef]
- 17. Periasamy, A.; Muruganand, S.; Palaniswamy, M. Vibrational Studies of Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, NaHSO<sub>4</sub> AND KHSO<sub>4</sub> crystals. *Rasayan J. Chem.* **2009**, *2*, 981–989.
- CrysAlisPro 1.171.38.46; Rigaku Oxford Diffraction: The Woodlands, TX, USA, 2015; Available online: https://www.rigaku.com/ products/crystallography/crysalis (accessed on 2 November 2022).
- 19. Sheldrick, G.M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8. [CrossRef] [PubMed]
- 20. Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Crystallogr. 2015, C71, 3–8. [CrossRef]