Probing Hydrogen-Bonding Properties of a Negatively Charged MoS₂ Monolayer by Powder X-ray Diffraction and Density Functional Theory Calculations

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ABSTRACT: The contributions of various noncovalent interactions in stabilization of the assembled and delaminated MoS₂–hexamethylenetetramine (HMTA)-layered compound resulted from the assembly of protonated HMTA molecules and negatively charged 1T-MoS₂ monolayers have been considered on the basis of powder X-ray diffraction pattern modeling, density functional theory calculations, and atoms in molecules quantum theory analysis. The structure with HMTA cations involved in NH···S bonding with MoS₂ layers was concluded to be more advantageous than the alternative one with NH···N bonding between the cations. Delamination was demonstrated to essentially influence the hierarchy of interactions and leads to significant strengthening of the NH···S hydrogen bond established between HMTA and the MoS₂ monolayer surface. The method applied in this study for evaluation of the monolayer MoS₂ properties on the basis of the 3D structure of the MoS₂–organic compound is expected to be helpful to gain insights into the interactions occurring in many MoS₂-based systems.

1. INTRODUCTION

Molybdenum disulfide, a well-known 2D material, has become the object of high-priority investigations because of its outstanding physicochemical properties interesting for modern nanoelectronics, energy storage, and photo(electro)-catalysts.¹⁻⁴ The S–Mo–S monolayers with covalently bound Mo and S atoms are combined in the structure of molybdenum disulfide by van der Waals interactions.⁵ As shown previously, the negative charging of MoS₂ monolayers, often combined with addition of cationic or neutral organic species, allows the modification of the atomic and electronic structure of the material and can be used for tuning conducting/semiconducting, optical, electrochemical, or catalytic properties.⁶⁻⁸ Determination of the atomic scale structure and bonding interaction network of the charged monolayer or few-layer MoS₂ particles associated with organic molecules is of primary importance not only on a fundamental aspect of constructing MoS₂–organic systems but also from a progress in application of such systems for thin-layer transistors,⁹ sensors,¹⁰ and energy-storage devices.¹¹ For instance, the assignment of the geometry of the MoS₂ lattice in the hybrid structure to one of the two structural modifications (with a trigonal prismatic or octahedral Mo coordination polyhedron) indicates which type of conductivity (semiconducting or conducting) may be expected for this structure.¹² Knowing the interaction mechanism and the binding strength of peptides or nucleotides with the MoS₂ surface is expected to use such systems for biomedical applications.¹³⁻¹⁴

Investigation of bonding between the macroanionic MoS₂ monolayers and organic compounds requires definite structural models for the MoS₂–organic interface. It can be thought that the most realistic and comprehensive structural models for this purpose can be derived from the structure of layered compounds of MoS₂ with organic species. Such compounds, having a reproducible stoichiometry and containing regularly alternating monolayers of negatively charged MoS₂ and organic cationic molecules, have been known for a long time; they are easily accessible by liquid-phase assembling.⁶,¹⁵ The only difficulty for their application in structural modeling is the turbostratic disorder, limiting the available structural information. The problem, however, has recently been overcome with the new combined powder X-ray diffraction (PXRD) and density functional theory (DFT) computation approach, which consists in diffraction pattern modeling of turbostatically disordered solids with the K. Ufer supercell¹⁶ and optimization of the models by quantum-chemical calculations.¹⁷ This approach has already allowed successful estimation of the structure of MoS₂ compounds with quaternary alkyl(aryl)-ammoniums, naphthylammoniums, and alkylamidammoniums.¹⁸⁻²⁰ The distinctive feature of these compounds is the existence of H-bonding interactions of various strengths between the S atoms of MoS₂ and molecular fragments. Obviously, a similar set of hydrogen bonding interactions can be expected on the surface of MoS₂ because hydrogen bonding typically governs the binding of organic species with the surfaces-containing donor atoms such as O or S.
It appeared to be interesting to gain new insights into the hierarchy of MoS₂−organic H-bonding interactions at the surface and interface of MoS₂-based materials by studying the layered system with concurrent types of strong hydrogen bonding not only between the MoS₂ layer and molecule as in previously studied systems but also between the molecules within the organic layer. For the role of such system, we chose the compound of MoS₂ with protonated hexamethylenetetramine (HMTA) (Figure 1) having four amino basic centers in its polycyclic C−N skeleton,²¹ the known agent for the self-assembly of supramolecular architectures.²²

![Protonated HMTA molecule structure (a) and its space-filled representation (b) with additional hydrogen atom shown in violet color.](Image 120x553 to 240x615)

To tailor the obtained structural model of the layered compound for examination of the phenomena at the surface of charged MoS₂, we simulated delamination of the compound and compared the binding of the HMTA molecule embedded into the interlayer space of MoS₂ with binding of the same molecule associated with the only one MoS₂ layer. For both situations, the question of how MoS₂−organic interatomic interactions influence the structural properties of the negatively charged MoS₂ lattice was of particular concern. To shed light on all these questions, the structure of HMTA−MoS₂ layered compound prepared via the assembly process was determined by the combined PXRD and DFT study analyzed in the framework of the quantum theory of atoms in molecules (QTAIM)²３ and used in modeling of monolayer MoS₂ interactions.

2. RESULTS AND DISCUSSION

2.1. Structure Determination of the HMTA−MoS₂ Compound. The assembly of negatively charged MoS₂ layers dispersed in water and HMTA molecules results in precipitation of the HMTA−MoS₂ compound in the form of lamellar structures. Regular alternation of the organic and MoS₂ layers in this structure was reliably estimated by the previous transmission electron microscopy (TEM) study.²⁴ Taking into account the acidity of the reaction medium, the organic layers can be assumed to contain HMTA molecules in a monoprotonated form, the only stable protonated form of this organic compound.²⁵ The HMTA-to-MoS₂ molar ratio (x) in the reaction product (eq 1) determined by elemental analysis thus corresponds to the amount of negative charge remaining on the MoS₂ layers (0.24 e/Mo).

\[
(MoS₂)^{x⁻} + A^+ \rightarrow A^+_x(MoS₂)^{x⁻}
\]  

(1)

The PXRD pattern of the compound shows clear evidence of the interlayer lattice expansion by ~5.5 Å due to the incorporation of HMTA moieties between the MoS₂ sheets, evinced by the positions of 00l reflections, shifted to low-angle values as compared to the initial MoS₂ (Figure 2).

As with the several previously studied MoS₂ compounds, the pattern of the present HMTA−MoS₂, with narrow 00l and broad hk0 reflections caused by two-dimensional ordering in the layers and aperioicity in their stacking, has a obvious similarity with the patterns of turbostratically disordered clays, the quantitative modeling of which using the supercell approach was previously developed by Ufer.₁⁶ The method applied for the fit comprises an increase in the unit cell dimension along the direction of structural disordering (the c-axis, in our case) by N times in order to reproduce the measured 00l reflections by the 00l, reflections of the virtual supercell (l₁ = N × l) and to describe simultaneously the hk0-zone by numerous hkl reflections of a supercell. This makes possible direct Rietveld refinement of the profile within the unified structural model. Modification of this approach was recently applied for hybrid MoS₂ compounds assuming that the elemental layer of a system contains a MoS₂ sheet with associated organic molecules.³⁷ Possible correlations in the relative positions of MoS₂ layers were accounted for supercell containing two hybrid MoS₂−organic layers with refineable relative positions.

To proceed with structure refinement, the starting models of MoS₂ and organic layers were defined as follows. The starting geometry of the MoS₂ layer was chosen to be similar to the geometry determined previously for the compounds containing MoS₂ layers bearing a partial negative charge of the similar value.₁⁷,₁₈,₂₀ For the initial geometry of the organic layer, two models were considered, accounting for alternative possibilities for protonated HMTA molecules to participate in intermolecular hydrogen bonding: with the S atoms of the sulfide sheet or with the N atoms of the neighboring HMTA molecules. This implies the formation of NH···S (str-H-S) or NH···N (str-H-N) hydrogen bonds, respectively. For str-H-S, Ufer’s supercell contained the uniformly oriented organic molecules with their N−H bond directed to the sulfide layer plane (Figure 3a). In case of str-H-N, structure refinement was performed with the cell containing the dimers of the guest

![Starting orientation of HMTA molecules in str-H-S (a) and str-H-N (b) differing in the direction of the N−H bond.](Image 4604 to 4610)
molecules attached to each other by the NH···N hydrogen bond as shown in Figure 3b.

### 2.2. Comparison of Structural Models with NH···S and NH···N Hydrogen Bonding

The most important structural characteristics of the compound determined by Rietveld refinement for both models are shown in Table 1. It is important to note that refinement of both models has led to the practically identical geometries of MoS2 sheets, coinciding mainly with the geometry of 1T-modification of MoS2. Its characteristic features are the surrounding of the Mo atoms by the distorted octahedrons of S atoms, the arrangement of the Mo atoms in zigzags running along the b-axis and the crimping of the S–Mo–S layers outer surface at a nanoscale level (Figure 4). It should be mentioned that the octahedral Mo–S coordination and diamond-like Mo chains are consistent with the features previously proposed for HMTA-intercalated MoS2 and monolayer 1T-MoS2, on the basis of high-resolution TEM and selected area electron diffraction data.  

The powder pattern modeling has not allowed us to choose between two models of HMTA involvement in hydrogen bonding. For both models, the calculated diffraction profile fits the experimental one quite well (Figures 2 and S1), showing nearly identical overall weighted profile R-factors, R_wp, amounting to 4.16% (str-H-S) and 4.09% (str-H-N). This can be explained by the similarity in the positions of the HMTA molecular core in the interlayer space for both models, which differ mainly in localization of an additional hydrogen atom (Figure 3). It is noteworthy that in both cases the refinement definitely converges to the HMTA molecule positions over the valleys formed by sulfur atoms on the sheet surface, providing the minimal interlayer lattice expansion of the MoS2 lattice (Figures 5a and 6a).

![Figure 4. Refined geometry of MoS2 sheets with ridges and valleys running along the b-axis.](image4.png)

![Figure 5. Optimized disposition of HMTA cations according to str-H-S, side view along the b-axis (a) and projection onto the MoS2 layer (b). Interatomic distances (Å) and interaction energies of the most strong contacts (kcal/mol, in parentheses) are indicated.](image5.png)
In case of str-H-N, the construction of the infinite chains of hydrogen-bonded cations from the dimers situated along the b-axis (the valley direction) was performed taking into account that the symmetry of the HMTA molecule does not permit the formation of a strictly linear chain from the dimers. Indeed, the third cation should be attached angularly to the dimer axis. In the periodic structure, the refined orientation of the dimeric species with respect to the MoS\(_2\) lattice can only be kept by placing the H-bonded dimers in the neighboring valleys. To form a hydrogen bond, these dimers should be shifted with respect to each other along the \(b\)-axis by 8.0 Å (2.5 \(\times\) \(b_0\), where \(b_0\) is a parameter of Ufer’s cell used in structure refinement). Interactions of the dimers with each other by means of H-bonds give the zigzag chain as shown in Figure 6b. The unit cell for the periodic crystal structure accounting for these chains and corresponding to the stoichiometry of the compound (1 mole of HMTA per 4 moles of MoS\(_2\)) has the following dimensions in the \(ab\) plane: \(\vec{b} = 4 \times \vec{b}_0\), \(\vec{a} = 2 \times \vec{a}_0 + \vec{b}_0\) (Table 1). Translation along the \(c\)-axis comprises the refined relative shifts of the MoS\(_2\) sheets with respect to each other and amounts to \(\vec{c} = \vec{c}_0 + \Delta_\alpha + \Delta_b\) (Table 1). The cell thus contains 4 HMTA cations, 16 Mo, and 32 S atoms.

As with the above-mentioned str-H-S, the optimized geometry of str-H-N closely resembled the starting one with only slight deviation in the relative positions of the HMTA cations in the chain. The N–N distances corresponding to intermolecular NH–N hydrogen bonding lie in the range 2.908–3.072 Å, and the NHN angles amount to 157°–162°. The selected structural parameters of the optimized crystal structures for both models are shown in Table 1.

### 2.4. Bonding Interactions in the Layered Compound

Analysis of the calculated electron energy distribution \(\rho(r)\) in the studied HMTA–MoS\(_2\) architecture in the framework of Bader’s QTAIM\(^{23}\) was performed in order to reveal the (3,–1) bond critical points (bcps), corresponding to the bonding interactions. The interaction strength was further evaluated by using known correlations of Espinosa, Mollins, and Lecomte between the binding interaction energy of the contact and the potential energy density at the bcp.\(^{25}\) Summaries of critical point properties for both hypothetically ordered structures are shown in Tables S1 and S2.

The interatomic interaction energies \(E_{\text{cont}}\) in HMTA–MoS\(_2\) summarized for each type of contacts are given in Table 2 (str-H-S) and Table 3 (str-H-N). According to these results,

### Table 2. Energies (kcal/mol per Mole of Cation) and Numbers of Bonding Interactions in the Structure with NH···S Bonding (str-H-S)

| Contact | Number of Contacts | \(E_{\text{cont}}\) |
|---------|-------------------|-----------------|
| NH···S  | 1                 | 11.4            |
| CH···S  | 14               | 10.8            |
| CH···N  | 3                 | 3.2             |
| H···H   | 4                 | 0.8             |
| Cation–MoS\(_2\) | 16             | 22.2            |
| Total   | 24               | 26.2            |

Each HMTA cation in str-H-S is bound to the MoS\(_2\) sheet by one strong NH···S hydrogen bond with the energy of 11.4 kcal/mol and by numerous weaker CH···S hydrogen bonds, contributing cumulatively 10.8 kcal/mol in stabilization energy. A tendency to establish the shortest CH···S contacts is thought to be the driving force for positioning the HMTA molecules in...
the valleys of the nanorelief, in particular, for the molecule side opposite to the NH···S bond. The interaction energies of these contacts are around 1 kcal/mol, the typical value for the alkyl substituents in the amines intercalated in MoS2. Notably, binding of the cation with the sulfide sheet in str-H-S (22.2 kcal/mol) is much stronger than binding with neighboring organic molecules (~4 kcal/mol).

In str-H-N, strong hydrogen bonding is realized within the HMTA layer by means of the NH···N bond of an energy of 9.1 kcal/mol (Table 3). The calculations for this model have revealed roughly equal energies of the cation···MoS2 and cation···cation interactions amounting to 13.4 and 12.0 kcal per mole of the cation, respectively. Among the former interactions, the decisive contribution is due to CH···S ones, providing an overall contact energy of 11.7 kcal/mol. Notice that this value is close to an overall energy of these interactions in str-H-S, consistently with the proximity of HMTA core to sulfur sublattice in both models.

2.5. Discrimination of Structural Models for the Layered Compound. Though both structural models provide comparable values of the total specific interaction energies of the cation with the surroundings, the models differ significantly in the cation···MoS2 binding energy (Tables 2 and 3). Its value is considerably stronger for str-H-S. The structural models also differ in the relative strength of the guest···MoS2 and guest···guest interactions. In this respect, str-H-S with the guest···MoS2 binding evidently dominated over the guest···guest one seems to be in better accord with the interaction hierarchy observed for the previously reported MoS2···organic compounds.19,20

Further discrimination of the models was made by considering the total energy values obtained by DFT calculations for each structure, $E_{\text{tot}}$, and reduced to 1 mole of HMTA cations, $E_{\text{int}}$ (Table 4). Evidently, these fundamental energetic characteristics are influenced not only by chemical bonding but also by Coulombic interactions, both the attractive and repulsive ones, appearing in the system with the negatively charged MoS2 sheets and positively charged guest cations. A significant role of electrostatic interactions in stabilization of one of the possible layered structures was recently demonstrated for MoS2···naphthylamine compounds.19 The difference in $E_{\text{int}}$ values between two models of the present layered compound, amounting to 10.4 kcal per mole of the HMTA cation, is the most important argument in favor of str-H-S with NH···S hydrogen bonding. It is also important to note that the electrostatic forces may also favor the observed strength of the NH···S interactions in str-H-S as compared to the NH···N ones in str-H-N because the former interactions are assisted by the opposite charges of the interacting species contrary to the NH···N bonds, which should be established between two cationic molecules. It can be inferred that NH···S bonding plays an important role from the early stages of the assembly process when separate HMTA molecules are binding to the MoS2 sheets. On the contrary, NH···N bonding of HMTA molecules implies more dense filling of the surface with the guest species.

2.6. Modeling of the Delaminated Compound. To gain new insights into the bonding properties of monolayer MoS2, we conducted delaminated models of HMTA···MoS2 layered compounds by hypothetical separation of MoS2···organic layers in the crystal structure by the vacuum layer as shown in Figure S2, using the procedure previously applied for the determination of the cohesion or exfoliation energy of hybrid layered compounds.19,28 This separation is assumed to make the interlayer interactions negligible and thus allows the detection of the intrinsic properties of the single MoS2 layer by using periodic DFT calculations and QTAIM analysis similar to the assembled compounds.

In delaminated models, we kept the stoichiometry of the layered compound and disposed the HMTA cations on both sides of the MoS2 monolayer surface (Figure 7). Previous studies showed that this disposition is a more energetically advantageous one than alternative one-side disposition.19,20 Two distances of layer separation was tested, ~3 and ~23 Å, which corresponded to the $c$-periodicity values of 20 and 40 Å, respectively. Examination of the total energy obtained after DFT optimization of delaminated models has revealed the small energy growth (by 0.1 kcal/mol) upon an increase in separation for more than 3 Å and an energy loss of 4.2–4.3 kcal/mol.

Table 3. Energies (kcal/mol per Mole of Cation) and Numbers of Bonding Interactions in the Structure with NH···N Bonding (str-H-N)

| contact | number of contacts | $E_{\text{int}}$ (kcal/mol) |
|---------|--------------------|------------------------------|
| NH···N  | 1                  | 9.1                          |
| CH···S  | 9                  | 11.7                         |
| N···S   | 2                  | 1.7                          |
| H···H   | 5                  | 2.9                          |
| cation···MoS2 | 11          | 13.4                         |
| total   | 18                 | 25.4                         |

Table 4. Energetic Characteristics of Assembled and Delaminated Models

| model     | $N^a$ | $E_{\text{tot}}$ (eV) | $E_{\text{int}}$ (eV)$^b$ | energy difference (kcal/mol)$^c$ |
|-----------|-------|-----------------------|----------------------------|----------------------------------|
| Assembled |       |                       |                            |                                  |
| str-H-S   | 1     | −219.520              | −219.520                   | 0                                |
| str-H-N   | 4     | −876.267              | −219.067                   | 10.4                             |
| Delaminated$^d$ |       |                       |                            |                                  |
| dm-H-S-20 | 2     | −438.679              | −219.339                   | 4.2                              |
| dm-H-S-40 | 2     | −438.669              | −219.335                   | 4.3                              |

$^a$Number of HMTA cations in the unit cell. $^b$Reduced to 1 HMTA cation. $^c$With the most energetically advantageous model. $^d$Numerals indicate the interlayer distance in Å.

Figure 7. Optimized disposition of HMTA cations in the delaminated model. Intertatomic distances (Å) and interaction energies of the strongest contacts (kcal/mol, in parentheses) are indicated.
kcal/mol with respect to the assembled compound (Table 5). Notice that the latter value is in fact the cohesion energy of the assembled structure previously defined as the minimal energy necessary for delamination of this structure.19

Table 5. Energies (kcal/mol per Mole of Cation) and Numbers of Bonding Interactions for the Delaminated HMTA–MoS2 Compound (dm-H-S-40)

| contact       | number of contacts | $E_{\text{int}}$ |
|---------------|--------------------|------------------|
| NH···S        | 1                  | 15.0             |
| CH···S        | 6                  | 4.2              |
| cation···MoS2 |                    | 19.2             |
| total         |                    | 19.2             |

The summary results of the topological analysis of the electron density and evaluation of the contact energy for the dm-H-S-40 structure are shown in Tables S3 and S5, respectively. Comparing the assembled and delaminated compound, one can see that in both cases the HMTA–MoS2 binding is realized by means of one NH···S and several CH···S contacts (Tables 2 and 5). However, the number of CH···S contacts is expectedly diminished after splitting because each molecule is now bound with only one MoS2 layer. Notice that the mean energy of these contacts does not change noticeably upon delamination. The important feature of the delaminated structure is the essential strengthening of the NH···S hydrogen bond. Its contact energy increases by ~30%, consistently with the decrease of the corresponding H–S distance by ~0.03 Å and increase of the NH angle from 165 to 173° (Table 6). The hydrogen bonding between MoS2 and the associated HMTA molecule is thus becoming an absolutely dominating interaction in the delaminated structure, which models the bonding properties expected for the single MoS2 layer.

3. CONCLUSIONS

By using the PXRD pattern modeling and DFT calculations, we determined for the first time the atomic structure of both the host and guest layers in the heterolayered MoS2–organic compound resulted from the self-assembly of MoS2 sheets bearing a partial negative charge and protonated HMTA molecules. For structure determination of the present compound complicated by the turbostratic disorder in the layer stacking and sphere-like shape of the guest molecule, two structural models satisfying the PXRD data were considered, which accounted for the participation of protonated HMTA in NH···S or NH···N hydrogen bonding. For both models, the structure of sulfdide sheets was found to correspond to the 1T modification of the MoS2 lattice. This modification, metastable per se, is preserved in this heterolayered structure due to conservation of the negative charge on the S–Mo–S layers owing to the incorporation of organic cationic molecules. DFT optimization and QTAIM analysis of structural models allowed us to characterize a set of bonding interactions appearing in each mode of hydrogen bonding and evaluate the energy of these interactions. Though the sum of the energies of the local interactions of the HMTA cation are approximately equal for both manners of hydrogen bonding, the structure with NH···S bonds assisted by the attractive charge interaction of the involved species is a much more advantageous one, as is evident from comparison of the total energy values of the corresponding structures.

Structural information obtained for the heterolayered HMTA–MoS2 compound was used for the creation of its delaminated models followed by the analysis of their structural and energetic characteristics. The essential strengthening of the NH···S hydrogen bond on delamination has been revealed, which is thought to reflect the tendency expected for hydrogen bonding of the MoS2 monolayer with the associated amino compounds. A similar approach can be applied for exploration of a wide range of MoS2–organic systems, which might be interesting for the application of monolayer MoS2 in various devices.

4. EXPERIMENTAL SECTION

4.1. Material Preparation. The powdered HMTA–MoS2–layered compound has been prepared by the self-assembly reaction as previously described using the single-layer aqueous dispersions of MoS2, containing negatively charged molybdenum disulphide (MoS2)− sheets and protonated HMTA molecules.24 Initially, the crystalline compound, LiMoS2, has been obtained by treating purified natural molybdenum disulphide (DM-1, Scopin Factory, Russia) with a particle size (95%) smaller than 7 μm with an excess of 1.6 M n-butyllithium solution in hexane (Aldrich) for 1 week, washing in hexane and drying in vacuum. This compound has been sonicated in bidistilled water to prepare aqueous dispersions of concentration 1 mg·mL−1. Then, 100 mL of the MoS2 dispersion has been mixed with 20 mL of the solution prepared by dissolution of HMTA (10 mol/mol MoS2) in water acidified by HCl. The reaction mixture was stirred on a magnetic stirrer for 2 h; the precipitate formed during the stirring was collected by centrifugation, washed by water, and dried in vacuum. The acidity of the first supernatant measured using the Hanna Instruments 8424 pH meter amounts to pH 4–5. The composition of the product was determined from the elemental analysis data (C, H, N, Mo). Found (calculated) for (C6H13N4)0.24MoS2: C 8.99 (8.91), N 6.22 (6.93), H 1.59 (1.60), Mo 48.25 (49.50).

4.2. Structure Refinement. The powder diffraction patterns were measured using a Bruker D8 Advance Vario diffractometer equipped with a Ge(111) Cu Kα monochromator and a LynxEye 1D silicon strip detector, in transmission between Kapton films. The measurement range was 6–90° 2θ, and the step size was 0.01° 2θ. All modeling and indexing was performed using TOPAS 4.2 software.

Table 6. Interatomic Distances ($d$), Angles and Energies of the NH···S Bond in the Assembled and delaminated Compound

| model | $d$ N–S (Å) | $d$ N–H (Å) | $d$ S–H (Å) | N–H–S (deg) | $E_{\text{int}}$ (kcal/mol) |
|-------|-------------|-------------|-------------|-------------|-----------------------------|
| str-H-S | 3.082       | 1.071       | 2.033       | 165.46      | −11.366                     |
| dm-H-S-40 | 3.049       | 1.097       | 1.956       | 173.12      | −15.066                     |
|       | 3.050       | 1.098       | 1.956       | 173.83      | −14.958                     |

The unit cell contains two independent cations.
The refinement of the \((\text{HMTA})_{0.23}\text{MoS}_2\) structure was performed using the X. Wang implementation\(^{29,30}\) for TOPAS 4.2\(^{31}\) of the “supercell approach” developed by Ufer et al.\(^{16}\) The factor of elongation \(N = 15\) was applied. For modeling, the primitive cell was used (space group \(P\)\(_1\)). The base unit cell consisted of two \(\text{MoS}_2\) and two organic layers; the relative shift of \(\text{MoS}_2\)–organic pairs was refined. The precise position of the HMTA cation was obtained by the refinement with anti-bump restraints on S–C contacts (minimum value of 3.4 Å). The cations were refined as rigid bodies, with an occupancy set from the chemical analysis data.

### 4.3. Quantum-Chemical Calculations

DFT (PW-PBE-D) periodic calculations were performed in the VASP package.\(^{32–35}\) Projector-augmented wave pseudopotentials\(^{36,37}\) were used for all atoms to describe core electrons. The contribution of valence electrons was described as series of PWs with a kinetic energy cutoff of 545 eV. Exchange and correlation terms of the total energy were described by PBE functional,\(^{38}\) with Grimme D3 dispersion correction.\(^{39}\) The correlation terms of the total energy were described by PBE functional,\(^{38}\) with Grimme D3 dispersion correction.\(^{39}\) The electron density function for the topological analysis was functional,\(^{38}\) with Grimme D3 dispersion correction.\(^{39}\) The electron density function for the topological analysis was obtained by the refinement with anti-bump restraints on S–C contacts (minimum value of 3.4 Å). Topological analysis was carried out by using the AIM program, a part of ABINIT software.\(^{40}\)

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04161.

Additional X-ray diffraction data, figures of delaminated models, bond critical point properties, and fractional coordinates of models (PDF)

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### Notes

The authors declare no competing financial interest.

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