Lactam/MoCl₅ interaction in CH₂Cl₂: synthesis and X-ray characterization of protonated δ-valerolactam salts

Fabio Marchetti,* Guido Pampaloni and Stefano Zacchini

The protonated lactam salts \( \text{HN(CH₂)₃C(OH)} \) \( \text{[MoOCl₄]} \), \( \text{[HN(CH₂)₃C(OH)} \) \( \text{[MoOCl₄]} \), \( \text{O=C(CH₂)₃NH} \), \( \text{2, and [H(\text{N(CH₂)₃C(OH)})]} \) \( \text{[MoOCl₄]} \), \( \text{O=C(CH₂)₃NH} \) \( ] \), \( \text{3, were isolated from the non selective reaction of MoCl₅ with δ-valerolactam in dichloromethane, carried out with different molar ratios. The 1 : 2 reaction of MoCl₅ with N-methyl-2-pyrrolidone afforded the chloroiminium salt (C(\text{N(CH₂)₃})\text{Me})[MoOCl₄(O=C(CH₂)₃\text{Me})] \), \( \text{4, in 74% yield, together with minor amount of MoCl₄(O=C(CH₂)₃\text{Me})]} \), \( \text{5, The products 1–5 were characterized by analytical and spectroscopic techniques, and by X-ray diffraction in the cases of 1 and 3.}}

Introduction

The proton-exchange reaction involving the N-bound hydrogen atoms of non cyclic amides has attracted large interest for its biologic implications. Alternative formation of O- or N-protonated cationic intermediates was postulated in order to account for the exchange. The studies were extended to small-ring cyclic amides (lactams), \( \text{HN(CH₂)₃C(O)} \) \( n = 3 \) to 6, for which it was outlined that the acid-catalyzed proton exchange proceeded via N-protonation in the cases of 2-pyrrolidinone \( (n = 3) \) and \( \varepsilon \)-caprolactam \( (n = 5) \). Instead the O-protonation mechanism was considered predominant for δ-valerolactam \( (n = 4) \) due to kinetic reasons.

Stable protonated lactams can be obtained by means of strong Brønsted acids such as \( \text{HX} \) \( (X = \text{Cl}, \text{Br}), \text{HNO₃} \) and \( \text{H}_₂\text{SO₄} \). This procedure allowed the isolation of a small number of protonated lactams which were characterized by X-ray diffraction.

In the course of our studies on the coordination chemistry of molybdenum pentachloride we have observed that chlorine–oxygen exchange is operative when a variety of amides (including DMF, acetanilide and \( \varepsilon \)-caprolactam) are allowed to react with MoCl₅ (Scheme 1). The resulting chloroiminium salts are generally isolable, although the presence of N-bound hydrogen in the amide reactant may determine successive intermolecular C–N coupling reaction via HCl release. In the case of acetanilide, the coupling takes place straightforwardly at room temperature and affords an acylanidinium derivative. Evidences for analogous, thermally-induced process have been collected for \( \varepsilon \)-caprolactam.

A parallel study on the chemistry of WCl₆ has furnished analogous results, and has pointed out that C–H bond activation is presumably one of the pathways operative in the interaction of the metal species with cyclic and non cyclic amides.

In the present paper, we report on the reactivity of MoCl₅ with δ-valerolactam and N-methyl-2-pyrrolidone in CH₂Cl₂ at room temperature. The reactions involving δ-valerolactam, carried out using different metal/lactam ratios, afforded salts containing the protonated lactam. This result is uncommon in that the protonation process here does not require the direct use of a strong protonating agent (see above). The unprecedented X-ray characterization of protonated δ-valerolactam salts will be presented.

\( ^{a}\text{University of Pisa, Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, 56126, Pisa, Italy. E-mail: fabmar@dcci.unipi.it; Tel: +39 0502219245} \)
\( ^{b}\text{University of Bologna, Dipartimento di Chimica Industriale "Toso Montanari", Viale Risorgimento 4, I-40136, Bologna, Italy} \)
\( ^{c}\text{CCDC 913341 (1) and 913342 (3). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra23305g} \)
Results and discussion

The 1 : 3 molar reaction of MoCl$_5$ with $\delta$-valerolactam in dichloromethane resulted in formation of a bright-green solution over a pale-green precipitate. The crystalline compound [HN(CH$_2$)$_4$CO(OH)]$_2$[MoOCl$_5$], 1, was recovered in 35% yield from the solution after work-up (Scheme 2). Instead the precipitate was identified to be the complex [HN(CH$_2$)$_4$CO(OH)]_2[MoOCl$_5$(O=C(CH$_2$)$_2$NH)] Cl, 2. The latter was obtained in better yield by allowing MoCl$_5$ to react with $\delta$-valerolactam in 1 : 2 molar ratio (Scheme 2).

On the other hand, the reaction conducted with a five-fold molar excess of $\delta$-valerolactam allowed to isolate [HN(CH$_2$)$_4$CO(OH)]$_2$[MoOCl$_5$(O=C(CH$_2$)$_2$NH)] Cl, 3, in 28% yield (Scheme 2).

The protonated-valerolactam salts 1–3 were characterized by IR and NMR spectroscopy, magnetic susceptibility and elemental analysis. Moreover the X-ray molecular structures of 1 and 3 were ascertained: the ORTEP representations are shown in Fig. 1 and 2, whereas relevant bond lengths and angles are reported in Tables 1 and 2.

Compound 1 is made of one [MoOCl$_5$]$^{2-}$ anion and two [HN(CH$_2$)$_4$CO(OH)]$^+$ cations connected by hydrogen bonds (see Table 1 and Fig. 3a). In particular, the axial Cl(1) atom of the anion displays a relatively strong interaction with the O(2)–H(3) group of the cation [O(2) …Cl(1)#2 3.0037(14) Å], whereas the equatorial chlorides show weaker contacts with the N(2)–H(2) group [N(2) …Cl(4) 3.4260(18) Å; N(2) …Cl(3) 3.4249(17) Å].

The cationic part of 1 is represented by O-protonated valerolactam units, whose structural features are in good agreement with those reported for other crystallographically-characterized protonated lactams. With reference to the X-ray molecular structure of the seven-membered ring $\varepsilon$-caprolactam, the C(1)–O(2) distance in 1 is significantly elongated as result of O-protonation [1.305(2) Å in 1, 1.242 Å in $\varepsilon$-caprolactam; the corresponding value for $\delta$-valerolactam in the gas phase is 1.226 Å]. Conversely the C(1)–N(2) interaction appears sensibly shortened [1.291(2) Å in 1; 1.327 Å in $\varepsilon$-caprolactam]. Distances between adjacent methylene groups fall in within the range typical for Csp$^3$–Csp$^3$ interactions.
The Mo(1) centre is in a distorted octahedral environment and is 0.313 Å displaced from the least squares plane of four equatorial chloro ligands towards the oxo group. The Mo(1), Cl(1), Cl(2) and Cl(3) atoms lie on a crystallographic mirror plane. The bond distances Mo(1)–O(1) and Mo(1)–Cl eq are similar to those found in other known structures which contain monomeric [MoOCl 5]2– anions.14 The Mo(1)–Cl(1) bond [2.7582(7) Å], being trans to the oxo group, is significantly longer than the Mo(1)–Cl eq bonds [2.3741(7)–2.3820(7) Å]. The Mo–Cl axial distances usually found in other [MoOCl 5]2– salts fall in the range 2.533(5)–2.579(0) Å, the increase respect to the Mo–Cl eq distances being attributed to the trans effect of the oxo ligand.14 This feature alone does not account for the large elongation observed in 1, that is probably due to the strong H-bond involving Cl(1) and the OH group of the cation. A similar effect was found in the pyridinium salt [C5H5NH][MoOCl 5]2–CH2Cl2 [Mo–Cl axial 2.6910(6) Å], where a strong H-bond between Cl axial and the pyridinium cation was detected.14

The equatorial chlorides in 1 are involved in rather weak H-bonds and, thus, they display distances typically observed in [MoOCl 5]2– salts.14

The asymmetric unit of the unit cell of 3 contains one [MoOCl4(O= C(CH2)4NH) ]2– anion (on a general position), two [HN(CH2)3C(OH) ]2– cations (on general positions) and two halves of Cl2 anions (on 2 axis). As summarised in Table 2, several H-bonds are present involving the N–H and O–H groups of the cations as donors and the bonded and free chloride ions as acceptors (see Fig. 3b). The bonding parameters of the protonated valerolactam cations are as those found in 1. The molecular structure of the anion closely resembles those previously found for [MoOCl4(dmf)]–8 and [MoOCl4(MeCN)]–14b Thus, the anion displays a distorted octahedral geometry, with the ligand in trans position with respect to MoL(O). The Mo(1)–O(1) [1.6625(13) Å] and Mo(1)–O(12) [2.1892(12) Å] interactions are in agreement with a double and a single bond, respectively. The C(11)–O(12) distance [1.266(2) Å] resembles those recognized for the valerolactam ligands in 15 and in 16, respectively.

![Fig. 3](image-url) a) Hydrogen bonding in 1; b) hydrogen bonding in 3.

Table 2 Selected bond distances (Å) and angles (°) for 3

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<th>Bond</th>
<th>Distance</th>
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<tr>
<td>Mo(1)–O(1)</td>
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<td>Mo(1)–Cl(1)</td>
<td>2.3965(5)</td>
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<tr>
<td>Mo(1)–Cl(2)</td>
<td>2.3984(5)</td>
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<tr>
<td>O(12)–C(11)</td>
<td>1.266(2)</td>
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<td>C(15)–N(1)</td>
<td>1.480(2)</td>
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<td>O(1)–Mo(1)–O(12)</td>
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<td>3.2964(17)</td>
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<tr>
<td>Cl(1)–Mo(1)–Cl(3)</td>
<td>168.40(17)</td>
<td>3.1511(13)</td>
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<td>O(12)–C(11)–N(1)</td>
<td>112.32(17)</td>
<td>3.1530(3)</td>
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<td>N(1)–C(11)–C(12)</td>
<td>119.44(16)</td>
<td>3.1534(3)</td>
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<tr>
<td>C(11)–N(1)–C(15)</td>
<td>126.56(17)</td>
<td>3.1534(3)</td>
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<tr>
<th>Hydrogen Bonds</th>
<th>D–H···A</th>
<th>D–H</th>
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<tr>
<td>N(1)–H(1)–Cl(1)</td>
<td>0.846(16)</td>
<td>2.529(18)</td>
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<td>0.854(15)</td>
<td>2.682(2)</td>
<td>3.3432(17)</td>
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<td>N(2)–H(2)–Cl(3)#1</td>
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<td>O(32)–H(32)–Cl(6)#2</td>
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<td>0.836(15)</td>
<td>2.541(16)</td>
<td>3.3579(17)</td>
<td>166(2)</td>
</tr>
</tbody>
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* Symmetry transformations used to generate equivalent atoms: #1: –x + 1, –y + 1, –z + 1; #2: x – 1, y, z.
The IR spectra of 1–3 in the solid state display a strong absorption at 1670–1690 cm\(^{-1}\), which was previously assigned to the \([\text{N}–\text{C}–\text{O}]\) frame in protonated \(\delta\)-valerolactam.\(^{26}\) Otherwise the absorption falling at ca. 1620 cm\(^{-1}\) in the IR spectra of 2 and 3 is ascribable to the coordinated carbonyl.\(^{17}\) The Mo–O moiety manifests itself by a strong band at 980–1000 cm\(^{-1}\).\(^{7,8}\)

The magnetic susceptibility values obtained for 1–3 are in agreement with previous findings concerning \(\text{[Mo}^{\text{V}}\text{OCl}_4]^-\) derivatives.\(^{9,18}\)

The protonated valerolactam cation in 1–3 could be characterized in \(\text{CD}_3\text{CN}\) solution by NMR spectroscopy. Broad resonances in the \(^1\text{H}\) NMR spectrum were assigned to NH and OH protons (e.g. at 8.70 and 8.07 ppm in the case of 1).\(^{19}\) Major feature concerning the \(^1\text{C}\) spectrum regards the carbonyl carbon, that resonates at ca. 180 ppm, i.e. slightly low field shifted with respect to what seen in \(\delta\)-valerolactam.\(^{20}\) The methylene carbons in 1 have been found at 47.6, 32.6, 23.2, 21.5 ppm.

According to our recent reports about the reactivity of \(\text{MoCl}_5\) with amides (Scheme 1),\(^7\) the oxo ligand in 1 probably originates from chlorine–oxygen exchange between the metal centre and a portion of the organic reactant. The same process has been demonstrated previously for the analogous reaction of \(\text{MoCl}_5\) with \(\varepsilon\)-caprolactam. In order to identify the counterpart of the exchange process, we analyzed the content of the reaction solution by IR (solid state) and NMR (\(\text{CDCl}_3\) solution) spectroscopy. Unfortunately these analyses did not provide useful information. In fact the IR spectrum pointed to the presence of a mixture of compounds, while the paramagnetism associated with the metal species represented a non overcoming drawback for the NMR characterization.

We hypothesize that the activation of the N–H bond belonging to an aliquot of the organic reactant is a possible proton source for the formation of the protonated lactam ions in 1–3. Indeed we have already demonstrated that such kind of activation may be operative in the interaction of \(\text{MoCl}_5\) with lactams (Scheme 1).\(^{7,8}\) Also lactam C–H bond activation may occur to some extent and contribute to the protonation, analogously to what was reported for the parallel chemistry involving \(\text{WCl}_6\) (see Introduction).\(^9\) Finally the contribution of the protic solvent and traces of water should not be ruled out.

In order to deepen this point, we extended the present study to the reactivity of \(\text{MoCl}_5\) with \(N\)-methyl-2-pyrrolidone. The 1 : 2 molar reaction, carried out in conditions similar to those described for the synthesis of 1–3, resulted in the formation of a mixture consisting of a green solution and an ochre-yellow precipitate (Scheme 3). The former, that corresponded to the largely prevalent component of the mixture, was dried under \textit{vacuo} thus affording a green powdery material. Magnetic susceptibility, elemental analysis and IR spectroscopy suggested the formation of \(\text{[Cl}^{\text{[CH}_2]^3}\text{NH}\text{][MoOCl}_4\{\text{O}^{\text{[CH}_2]^3}\text{NH}\}\}}\), 4. The IR spectrum of 4 displays a broad, intense absorption in the carbonyl region (at 1622 cm\(^{-1}\)), attributed to the \([\text{C}–\text{O}]\) and \([\text{C}═\text{N}^{\text{iminium}}]\) stretching vibration modes, in analogy with what reported for the X-ray characterized \(\text{[Cl}^{\text{[CH}_2]^3}\text{NH}\text{][MoOCl}_4\{\text{O}^{\text{[CH}_2]^3}\text{NH}\}\}}\) salt (see Scheme 1). Instead the ochre-yellow precipitate, obtained in low-yield, was identified as the \(\text{Mo}^{(\text{IV})}\) species \(\text{MoCl}_4\{\text{O}^{\text{[CH}_2]^3}\text{NMe}\}\}\). 5. The magnetic susceptibility measurement for 5 resembles the data available for \(\text{MoCl}_4\) derivatives.\(^{7b,8b}\) In the IR spectrum, the carbonyl band has been found at 1657 cm\(^{-1}\). The \(^1\text{H}\) NMR spectrum of 5 (in \(\text{CD}_3\text{CN}\) solution) is as follows: 4.15 (br, \(\text{CH}_2\)), 3.49 (br, \(\text{NMe}\)), 2.36 (br, \(\text{CH}_2\)), 2.07 (br, \(\text{CH}_2\)) ppm.

The reaction of \(\text{MoCl}_5\) with \(N\)-methyl-2-pyrrolidone (\textit{i.e. a lactam missing of N-bound hydrogen}) appears to proceed with good selectivity to give the chlorine–oxygen exchange product 4. This outcome supports the hypothesis that the activation of the \(\delta\)-valerolactam N–H bond plays some role in the formation of O-protonated products upon reaction with \(\text{MoCl}_5\).

Conclusions

The synthesis and the isolation of different protonated-lactam salts have been achieved by the reactions of \(\delta\)-valerolactam with molybdenum pentachloride, in dichloromethane medium. In spite of the moderate yields of these reactions, due to low degree of selectivity, two points deserve to be remarked. Hence the unprecedented X-ray characterization of protonated \(\delta\)-valerolactam has been presented herein: the protonation site is the oxygen atom, in accordance with previous X-ray and theoretical findings. The other point of interest is that, at variance to what reported in the literature, the protonation process does not require the \textit{direct} use of a strong Brønsted acid, but it is promoted by the Lewis acidity of molybdenum pentachloride. A parallel study on the reactivity of \(\text{MoCl}_5\) with \(N\)-methyl-2-pyrrolidone did not lead to the isolation of protonated lactam products, thus suggesting that the possible activation of the NH moiety in \(\delta\)-valerolactam plays an important role in the low-yield \(\text{MoCl}_5\)-mediated protonation process.

Experimental

General

The reaction vessels were oven-dried at 120 °C prior to use, evacuated (10\(^{-2}\) mmHg) and then filled with dinitrogen. Molybdenum pentachloride was purchased from Strem (99.6%...
purity) and stored as received in sealed glass tubes under argon atmosphere. Once isolated, the metal products were conserved in sealed glass tubes under dinitrogen. δ-valerolactam and N-methyl-2-pyrrolidone were commercial products (Sigma-Aldrich) stored under dinitrogen as received. Solvents (Sigma-Aldrich) were distilled before use from appropriate drying agents. Infrared spectra were measured on solid samples at 298 K with Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diagnamagnetic corrections were introduced according to König. NMR spectra were recorded at 293 K on Bruker Avance DRX400 instrument equipped with BBFO broadband probe. The chemical shifts for 1H and 13C were referenced to DMSO-d6. 1H NMR (CD3CN): δ = 7.65 ppm. 13C{1H} NMR (CD3CN): δ = 133.0 ppm. 

Synthesis and isolation of [HN(CH2)2C(OH)]2·[MoOCl5]3, 1, and [HN(CH2)2C(OH)]·[MoOCl4·O=C(CH2)2NH]4, 2

A suspension of MoCl5 (0.205 g, 0.750 mmol) in CH2Cl2 (15 mL) was treated with δ-valerolactam (0.209 mL, 2.25 mmol). The mixture was stirred for 18 h at room temperature, then the resulting bright-green solution was filtered in order to separate it from a pale-green powder (2) which was dried under vacuo. Yield: 0.109 g, 28%. Anal. Calcd for C15H29Cl5MoN3O4: C, 30.61; H, 4.97; N, 7.14; Cl, 30.12. Found: C, 30.34; H, 5.12; N, 7.06; Cl, 29.62. IR (solid state): 2922 w-br (νC–H + νO–H), 2907 w, 1657 vs (νC–O), 1459 w, 1443 w, 1402 m, 1336 s, 1289 w, 1262 m, 1227 m-w, 1123 m, 1098 m, 1015 w, 730 vs cm−1. Magnetic measurement: χMcorr = 1.15 × 10−3 cm3 mol−1 K−1. 1H NMR (CD3CN): δ = 10.80, 8.20 (br, NH + OH), 3.41, 2.50, 1.87 (br, CH2) ppm.

Synthesis and isolation of [Cl(C2H3)2NMe]·[MoOCl4·O=C(CH2)2NMe]4, 3, and [MoOCl4·O=C(CH2)2NMe]5, 4

The reaction of MoCl5 (0.350 g, 1.28 mmol) with N-methyl-2-pyrrolidone (0.250 mL, 2.59 mmol) in CH2Cl2 (20 mL) was carried out by a procedure similar to that described for the synthesis of 1 and 2. An ochre-yellow precipitate (5) from a green solution was obtained and dried under vacuo. Yield: 0.447 g, 74%. Anal. Calcd for C21H23Cl5MoN5O: C, 17.83; H, 2.69; N, 4.16; Cl, 42.10. Found: C, 17.66; H, 2.81; N, 4.03; Cl, 41.98. IR (solid state): 2958 w-br (νC–H + νO–H), 2907 w, 1657 vs (νC–O), 1459 w, 1443 w, 1402 m, 1336 s, 1289 w, 1262 m, 1227 m-w, 1123 m, 1098 m, 1013 w, 730 vs cm−1. Magnetic measurement: χMcorr = 2.00 × 10−3 cm3 mol−1 K−1. 1H NMR (CD3CN): δ = 4.15 (br, CH2), 3.49 (br, NMe), 2.36 (br, CH2), 2.07 (br, CH2) ppm.

The green solution was dried under vacuo thus affording a dark-green powder corresponding to 4. Yield: 0.447 g, 74%. Anal. Calcd for C21H23Cl5MoN5O2: C, 25.48; H, 3.85; N, 5.94; Cl, 37.60. Found: C, 25.23; H, 3.99; N, 5.80; Cl, 37.38. IR (solid state): 2922 w-br (νC–H + νO–H), 2885 w, 1622 vs-br (νC–O + νC–N), 1599 s, 1477 w, 1448 w, 1407 m, 1310 m, 1257 m, 1230 w, 1116 m, 1092 w, 1045 w-m, 968 vs (νMo=O), 943 m, 849 m, 803 m, 755 s, 674 m-s cm−1. Magnetic measurement: χMcorr = 1.09 × 10−3 cm3 mol−1 K−1. 1H NMR (CDCl3): δ = 4.0 (br, NMe + CH2), 3.24 (br, CH2), 2.33 (br, CH2) ppm.

X-Ray crystallography

Crystal data and collection details for 1 and 3 are reported in Table 3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS). Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F2.24 All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions, except N and O bonded H-atoms which were located in the Fourier map. The N–H and O–H distances were restrained to 0.89 and 0.87 Å, respectively, (s.u. 0.02) during refinement. H-atom were treated isotropically using the 1.2 (for N–H) and 1.5 (for O–H) fold Uiso value of the parent.
Atoms. Similar U restraints (s.u. 0.01) were applied to the C atoms in 3.

The asymmetric unit of the unit cell of 1 contains half of a [MoOCl₅]²⁻ dianion (on m), one [HN(CH₂)₂C(OH)]⁺ cation (on a general position) and half of a CH₂Cl₂ molecule (on m).

The asymmetric unit of the unit cell of 3 contains one [MoOCl₄(O–C(CH₂)₂NH)]⁻ anion (on a general position), two [HN(CH₂)₂C(OH)]⁺ cations (on general positions) and two halves of Cl⁻ anions (on 2 axis). Two CH₂ groups of one of the two independent cations are disordered over two positions and, therefore, they have been split and refined with one occupancy factor; also the H-atoms of the two CH₂ groups directly bonded to them have been included in the disorder model and, thus, split into two images.

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