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Crystalline-state photoreaction of a newly prepared organorhodium dithionite complex with *n*-hexyltetramethylcyclopentadienyl (Cp^{Hex} : $\eta^5\text{-C}_5\text{Me}_4n\text{-Hexyl}$) ligands was studied by single crystal X-ray diffraction experiments; $2\pi/5$ rotation of the Cp^{Hex} ligand is induced by the photoisomerization of the dithionite group ($\mu\text{-O}_2\text{SSO}_2$).

In the crystalline state, molecules are packed closely to each other and movement of the molecular components is restricted due to strong intermolecular interactions. Therefore, reactive crystals with large structural changes, which are promising candidates for developing new functional crystals,¹ tend to lose their crystallinity after the reaction; how to manage the local stress generated by the reaction is one of the fundamentally important issues in crystal engineering. Although many successful examples are reported to date,^{1–3} it remains difficult to retain crystallinity during and after the reaction.

In this context, we have found that, in the crystalline state, a rhodium dinuclear complex $[(\text{RhCp}^{\text{Me}})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)]$ (1^{Me}) with a photoreactive dithionite ($\mu\text{-O}_2\text{SSO}_2$) and two Cp^{Me} ($\eta^5\text{-C}_5\text{Me}_5$) ligands shows a fully reversible photochromic reaction with conversion to the corresponding $\mu\text{-O}_2\text{SOSO}$ complex (Fig. 1a).^{3a} In this system, the flat disk-like Cp^{Me} ligands undergo $2\pi/5$ jumping motions, *i.e.*, “rotational motion”, around the ligand–metal coordination C_5 axis,⁴ and the rotational motion of the Cp^{Me} ligands is coupled to the photochromic reaction.^{3a} This would be an essential factor for releasing the local stress induced by the photochromic reaction and for retaining the crystallinity. In the case of 1^{Et} , the rotational motion of the Cp^{Et} ($\eta^5\text{-C}_5\text{Me}_4\text{Ethyl}$) ligands having a protruding ethyl group is suppressed in comparison

Molecular motion in organometallic crystals: photoinduced $2\pi/5$ rotation of *n*-hexyltetramethylcyclopentadienyl ligand†

Hidetaka Nakai, * Yuu Kajiwarra and Seiya Miyata

with that of Cp^{Me} .^{3c} As a result, the photoreaction can initiate unique surface morphology changes, but the crystal collapses and loses its crystallinity upon prolonged photoirradiation. In the case of 1^{Pro} , although the Cp^{Pro} ($\eta^5\text{-C}_5\text{Me}_4n\text{-Propyl}$) ligands having a protruding *n*-propyl group can not experience the rotational motion, flipping motion of an ethyl moiety of the *n*-propyl group in the Cp^{Pro} ligand releases the local stress and contributes to retaining the crystallinity during the reaction.^{3b,e} Thus, in the crystalline state, the rotation of the Cp^{R} ligand having the protruding R groups is restricted significantly; this is also true for similar molecular systems.^{4,5}

In our efforts to manage the local stress in the photoreactive crystals by flexible long alkyl groups,⁶ we have now prepared a new organorhodium dithionite complex with *n*-hexyl groups $[(\text{RhCp}^{\text{Hex}})_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)]$ (1^{Hex} , Cp^{Hex} =

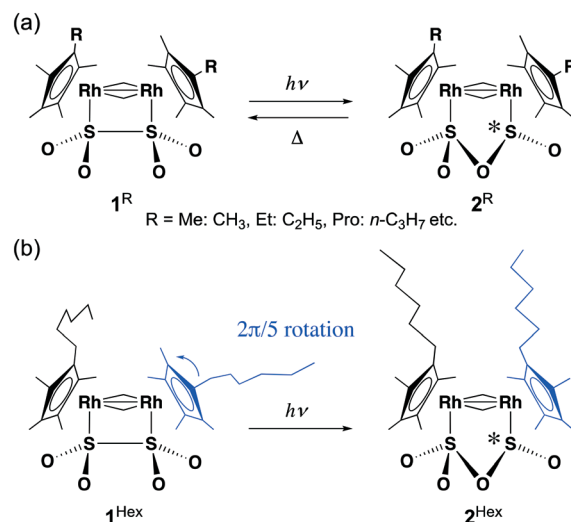


Fig. 1 (a) Photochromism of rhodium dithionite complexes, 1^{R} (R = Me, Et and Pro) and (b) crystalline-state photoreaction of 1^{Hex} . Photogenerated isomers 2^{R} have an asymmetric sulfur atom labelled *. The Cp^{Hex} ($\eta^5\text{-C}_5\text{Me}_4n\text{-Hexyl}$) ligands, which show the $2\pi/5$ rotation in the crystalline state, are indicated in blue. The blue arrow indicates the direction of the rotation.

Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, 3-4-1 Kowakae, Higashi-Osaka 577-8502, Japan.

E-mail: nakai@apch.kindai.ac.jp; Fax: +81 6 6721 2024; Tel: +81 6 6721 2332

† Electronic supplementary information (ESI) available: Experimental details, Tables (S1 and S2), and Fig. (S1–S3). CCDC 2054887 (1^{Hex}) and 2054888 (2^{Hex}). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ce00093d

$\eta^5\text{-C}_5\text{Me}_4n\text{-Hexyl}$) and surprisingly found that, in the crystalline state, $2\pi/5$ rotation of the Cp^{Hex} ligand having the protruding $n\text{-hexyl}$ group is induced by the photoisomerization of the $\mu\text{-O}_2\text{SSO}_2$ ligand (Fig. 1b); together with this unusual rotation, the $n\text{-hexyl}$ groups are re-oriented structurally. Herein, we report successful observation of the molecular motion found in the crystals of 1^{Hex} by using single crystal X-ray diffraction experiments.

The rhodium dithionite complex 1^{Hex} was newly synthesized by a method similar to that for 1^{R} using the Cp^{Hex} ligands instead of Cp^{R} (see the ESI†).³ Crystals of 1^{Hex} suitable for X-ray diffraction study were grown from a mixture of ethyl acetate and methylene chloride solution in the dark at room temperature. The shape and the molecular packing of the crystal of 1^{Hex} are shown in Fig. 2a.

The solid-state molecular structure of 1^{Hex} is depicted in Fig. 3a. In the crystal of 1^{Hex} , two crystallographically independent Cp^{Hex} ligands are locked in place by the surrounding Cp^{Hex} ligands of neighboring molecules. From the side view of 1^{Hex} , it can be recognized that the $n\text{-hexyl}$ groups on the front and back Cp^{Hex} ligands do not overlap each other in the crystalline state. The bond lengths and angles of the $\{\text{Rh}_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)\}$ core fragments of 1^{Hex} are similar to those found in 1^{R} . For instance, the S–S bond distances, which reflect the photoreactivity of the $\mu\text{-O}_2\text{SSO}_2$ ligand,^{3a} in 1^{Hex} , 1^{Me} and 1^{Et} are 2.3228(11), 2.330(2) and 2.351(2) Å, respectively.³

Upon irradiation with the light of an LED lamp (420–750 nm, 0.4 mW cm^{-2}) at room temperature, the red-orange crystals of 1^{Hex} changed to yellow-orange crystals of the $\mu\text{-O}_2\text{SOSO}$ complex 2^{Hex} (Fig. 1b and S1, ESI†).^{7–9} Although the essentially 100% interconversion ratio of the reaction from 1^{Hex} to 2^{Hex} in the crystalline state was confirmed by NMR and FT-IR spectra of the sample before and after photoirradiation (Fig. S2 and S3, ESI†), the crystal integrity was not preserved during the photoreaction.

Fortunately, some fragments of the after photoirradiation crystals of 1^{Hex} were found suitable for X-ray diffraction study. After the photoirradiation, the unit cell parameters change obviously. Especially, the length of the c -axis in the unit cell increased by 1.4% from 37.5526(10) to 38.0935(15) Å (Table S1, ESI†). The crystallographic c -axis is parallel to the shortest edge of the plate crystal (Fig. 2). This means that the degradation of the photoirradiated crystal is mainly caused by the expansion along the shortest edge of the plate crystal.

The solid-state molecular structure of 2^{Hex} is depicted in Fig. 3b. Disorder analyses of the oxygen atoms in Fig. 3b were similarly carried out to those done in 2^{R} ($\text{R} = \text{Me}$ and Pro) and indicated that the photoreaction from 1^{Hex} to 2^{Hex} takes place with an essentially 100% interconversion ratio in the crystal (unconverted starting complex only exists at $2 \pm 2\%$).¹⁰ It was also found that four species $2a^{\text{Hex}}\text{--}2d^{\text{Hex}}$ that cause the positional disorder of the oxygen atoms are generated with respective yields of 9, 86, 3 and $0 \pm 2\%$ (Fig. 4 and Table S2, ESI†); although the crystal has mirror images of $2a^{\text{Hex}}\text{--}2d^{\text{Hex}}$ as a set, in the present treatment, only one mirror image in the

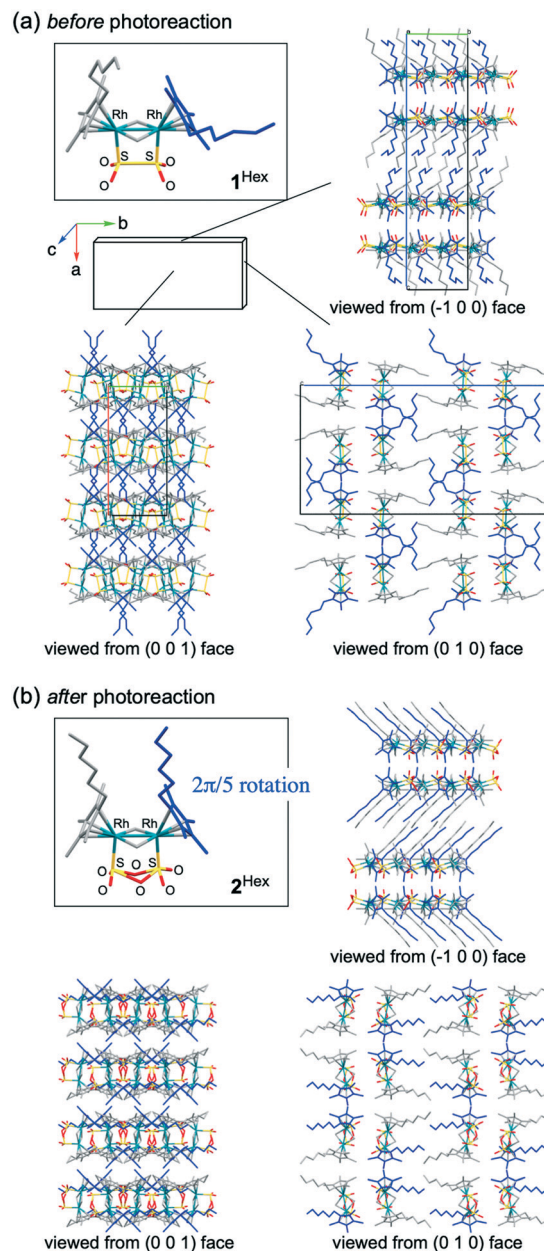


Fig. 2 Molecular packing diagrams of (a) 1^{Hex} including illustration of the crystal and (b) 2^{Hex} . Inset: Capped stick drawings of (a) 1^{Hex} and (b) 2^{Hex} , in which the hydrogen atoms are omitted for clarity. The Cp^{Hex} ($\eta^5\text{-C}_5\text{Me}_4n\text{-Hexyl}$) ligands, which show the $2\pi/5$ rotation in the crystalline state, are indicated in blue.

crystal is considered. The most dominant isomer is $2b^{\text{Hex}}$. Thus, occupancy of the O2 atom is reduced in the crystal of 2^{Hex} .

Surprisingly, the $2\pi/5$ rotation of the Cp^{Hex} ligand having the protruding $n\text{-hexyl}$ group is observed in the crystalline state when the molecular structure of 1^{Hex} is compared with that of 2^{Hex} (Fig. 3): in contrast to the side view of 1^{Hex} , from the side view of 2^{Hex} , it can be recognized that the $n\text{-hexyl}$ groups on the front and back Cp^{Hex} ligands almost overlap each other.

A careful comparison of the crystal structure of 1^{Hex} with 2^{Hex} tells us that this rotational motion occurs to fill the space

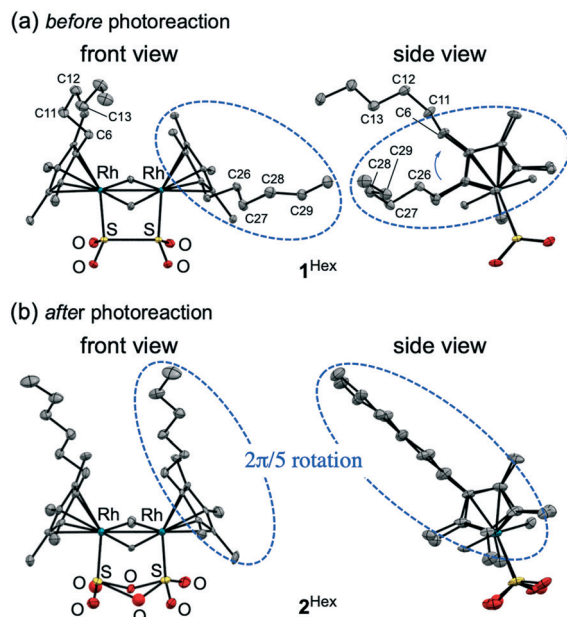


Fig. 3 ORTEP drawings of (a) 1^{Hex} and (b) 2^{Hex} with 50% probability ellipsoids. The hydrogen atoms are omitted for clarity. The Cp^{Hex} ($\eta^5\text{-C}_5\text{Me}_4n\text{-Hexyl}$) ligands, which show the $2\pi/5$ rotation in the crystalline state, are surrounded by blue dotted circles. The blue arrow indicates the direction of the rotation.

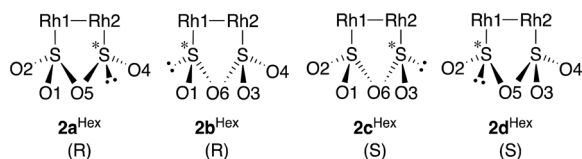


Fig. 4 The four stereoisomers, $2a^{\text{Hex}}$ – $2d^{\text{Hex}}$, concerned with the $\mu\text{-O}_2\text{SSO}_2$ unit. In the present treatment, only one mirror image in the crystal is considered. The Cp^{Hex} ($\eta^5\text{-C}_5\text{Me}_4n\text{-Hexyl}$) and $\eta\text{-CH}_2$ ligands are omitted for clarity. The absolute configurations of the sulfur atoms are shown in parentheses.

generated by oxygen atom transfer (Fig. 5). After the photoreaction, the C23 atom moves in the direction of the O2 atom: the distance between C23 and O2 changes from 3.810(5) to 3.15(6) Å. This is consistent with the fact that the isomer $2b^{\text{Hex}}$ formed by the O2 atom transfer is the main product of the crystalline-state photoreaction of 1^{Hex} (*vide ante*): the occupancy factors of the O2 atom change from 1.00 for 1^{Hex} to 0.14 for 2^{Hex} . These results support that the rotational motion is induced by the photoisomerization of the $\mu\text{-O}_2\text{SSO}_2$ ligand.

It is noteworthy that, as the photoreaction proceeds, the flexible *n*-hexyl groups of the Cp^{Hex} ligands are re-oriented structurally in the crystalline state (Fig. 2 and 3). Both the *n*-hexyl groups of the Cp^{Hex} ligands in 1^{Hex} (grey and blue in Fig. 2a and 3a) include one approximately *gauche* conformation; the dihedral angles of the C6–C11–C12–C13 and C26–C27–C28–C29 are 73.8(5) and 64.0(5)°, respectively. After photoreaction, both the *n*-hexyl groups in 2^{Hex} (grey and blue in Fig. 2b and 3b) become all-*trans* conformation.¹¹ The three-dimensional packing of 2^{Hex} is close to that of 1^{Hex} .

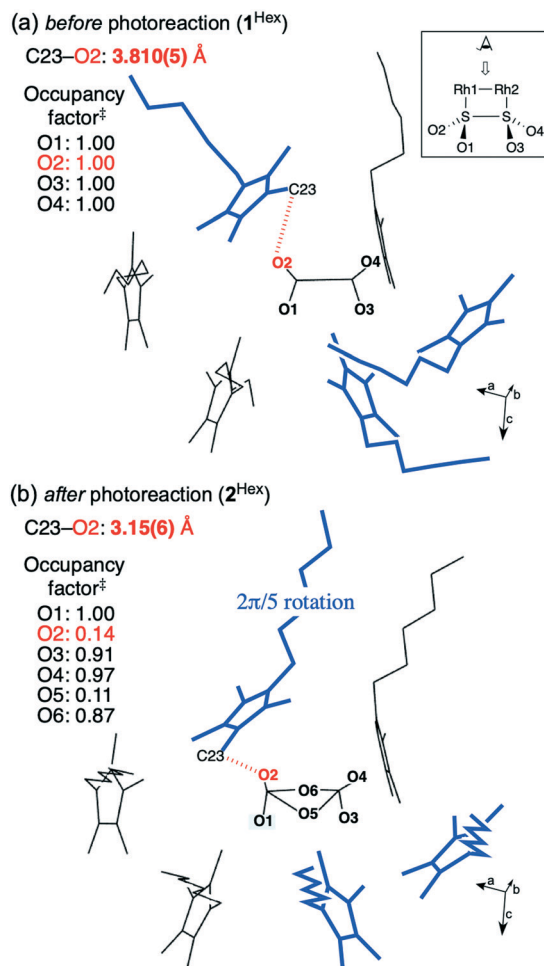


Fig. 5 Reaction cavities around the $\mu\text{-O}_2\text{SSO}_2/\mu\text{-O}_2\text{SOSO}$ unit in the crystals of (a) 1^{Hex} and (b) 2^{Hex} . The Cp^{Hex} ($\eta^5\text{-C}_5\text{Me}_4n\text{-Hexyl}$) ligands, which show the $2\pi/5$ rotation in the crystalline state, are indicated in blue. ‡ The significant decrease of the occupancy factor in O2 atom, which is due to the formation of $2b^{\text{Hex}}$ (Fig. 4), causes the $2\pi/5$ rotation of the blue Cp^{Hex} ligand.

These observations strongly indicate that, by moving of the flexible *n*-hexyl groups, (i) the unusual rotation of the Cp^{Hex} ligand is assisted and (ii) the local stress generated by the photoisomerization of the dithionite unit ($\mu\text{-O}_2\text{SSO}_2$) is released adequately. As a result, some fragments of the crystals can keep their crystallinity after the photoreaction.

In conclusion, we have demonstrated that the Cp^{Hex} ligand having the protruding *n*-hexyl group can experience the $2\pi/5$ rotational motion in the organometallic crystals. The flexible *n*-hexyl groups successfully assist the cramped rotation of the Cp^{Hex} ligand and adequately release the local stress generated by the photoisomerization of the dithionite group in the crystalline state. The cyclopentadienyl ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and pentamethyl-cyclopentadienyl (Cp^{Me}) derivatives are common and important ligands in organometallic chemistry.^{4,12} Thus, our findings not only provide attractive insights into the exploration/understanding of molecular motions in crystals but also offer new prospects for the construction of functional organometallic crystals.

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Conflicts of interest

There are no conflicts to declare.

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- In the case of 1^{Pen} (Pen: $n\text{-C}_5\text{H}_{11}$), the local stress induced by the photoisomerization is released by the disordering of the n -pentyl group of Cp^{Pen} ($\eta^5\text{-C}_5\text{Me}_4n\text{-Pentyl}$) ligand.^{3d}
- The absorption bands around 510 nm of the dithionite complexes can be assigned to the charge transfer band from the $\sigma(\text{S-S})$ to the $\sigma^*(\text{S-S})$ and $\sigma^*(\text{Rh-Rh})$ orbitals.^{3a}
- Although 2^{Hex} has an asymmetric sulfur atom (Fig. 1 and 4), the reaction gives pairs of enantiomers in the crystal (Table S2, ESI†).
- Upon heating of the crystal of 2^{Hex} , the back reaction occurs from 2^{Hex} to 1^{Hex} together with the slight color change. However, the crystal integrity is not preserved after the reaction: the obtained crystals are not suitable for X-ray diffraction study. Further studies to find the reaction conditions for retaining crystal integrity are now in progress.
- The S...S distance in 2^{Hex} is 2.926(3) Å which is similar to that found in 2^{Me} (2.964(3) Å).
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