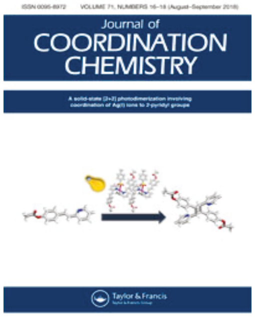


Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: https://www.tandfonline.com/loi/gcoo20

A solid-state [2 + 2] photodimerization involving coordination of Ag(I) ions to 2-pyridyl groups

Gonzalo Campillo-Alvarado, Katerina Aslan, Michael A. Sinnwell, Eric W. Reinheimer, S. V. Santhana Mariappan, Leonard R. MacGillivray & Ryan H. Groeneman

To cite this article: Gonzalo Campillo-Alvarado, Katerina Aslan, Michael A. Sinnwell, Eric W. Reinheimer, S. V. Santhana Mariappan, Leonard R. MacGillivray & Ryan H. Groeneman (2018) A solid-state [2+2] photodimerization involving coordination of Ag(I) ions to 2-pyridyl groups, Journal of Coordination Chemistry, 71:16-18, 2875-2883, DOI: 10.1080/00958972.2018.1501480

To link to this article: https://doi.org/10.1080/00958972.2018.1501480

JOURNAL OF COORDINATION CHEMISTRY
2018, VOL. 71, NO. 16-18, 2875–2883
https://doi.org/10.1080/00958972.2018.1501480

A solid-state [2 + 2] photodimerization involving coordination of Ag(I) ions to 2-pyridyl groups

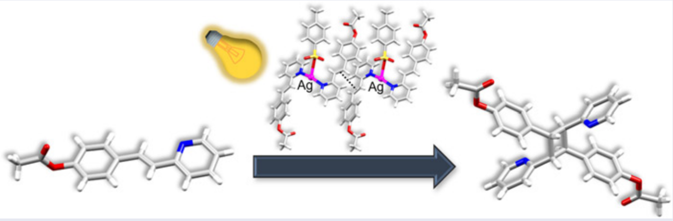
Gonzalo Campillo-Alvarado[a], Katerina Aslan[b], Michael A. Sinnwell[a], Eric W. Reinheimer[c], S. V. Santhana Mariappan[a], Leonard R. MacGillivray[a] and Ryan H. Groeneman[b]

[a]Department of Chemistry, University of Iowa, Iowa City, IA, USA; [b]Department of Biological Sciences, Webster University, St. Louis, MO, USA; [c]Department of Chemistry and the W.M. Keck Foundation Center for Molecular Structure, California State University, San Marcos, CA, USA

ABSTRACT

Photoreactive Ag(I) complexes of *p*-toluenesulfonate ions with the unsymmetrical alkene *trans*-1-(4-acetoxyphenyl)-2-(2-pyridyl)ethylene **1** is reported. The crystal [Ag(*p*-tol)(**1**)$_2$]•(H$_2$O) (*p*-tol = *p*-toluenesulfonate) undergoes a [2 + 2] photocycloaddition reaction in quantitative yield to afford the head-to-tail (ht) photoproduct *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-acetoxyphenyl)cyclobutane **2** regioselectively. The aromatic rings of the olefin participate in face-to-face π–π interactions and adopt an anti-conformation to position the carbon–carbon double bonds (C = C) in a suitable orientation to undergo photoreaction between neighboring complexes.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 27 March 2018
Accepted 5 June 2018

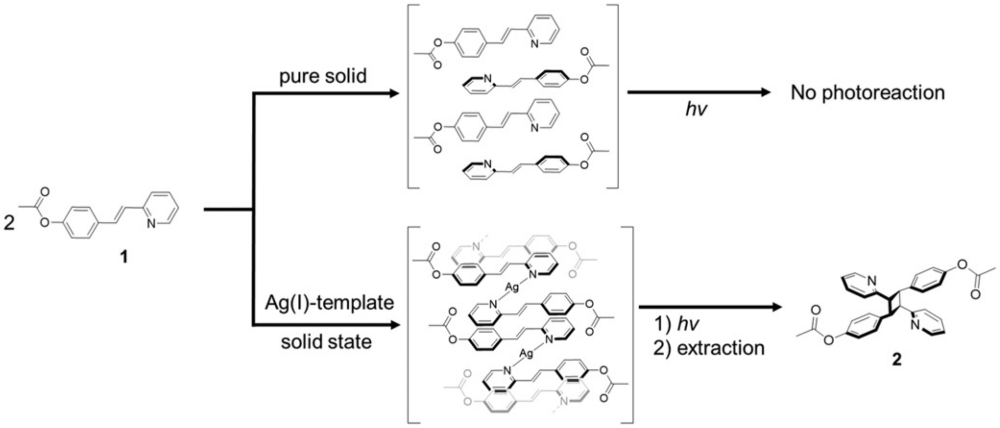
KEYWORDS
[2 + 2] Cycloaddition reactions; crystal engineering; head-to-tail photoproduct; silver organosulfonate; solid-state reactivity

1. Introduction

Within the last 15 years, numerous articles and reviews have highlighted a predilection of olefin-containing molecules to undergo [2 + 2] photocycloaddition reactions when organized in the solid state using template molecules or metal complexes [1–4]. In many cases, pyridine-containing reactants are employed to take advantage of the ability of the N-atom to accept hydrogen bonds and metal coordination bonds in the

CONTACT Leonard R. MacGillivray len-macgillivray@uiowa.edu Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA; Ryan H. Groeneman ryangroeneman19@webster.edu Department of Biological Sciences, Webster University, St. Louis, MO 63119, USA

Supplemental data for this article can be accessed at https://doi.org/10.1080/00958972.2018.1501480



Scheme 1. Synthetic strategy for synthesis of photoproduct **2** from a [2 + 2]-photocycloaddition reaction of crystalline [Ag(*p*-tol)(**1**)$_2$]•(H_2O).

former and latter, respectively. The strategy is used to assemble carbon-carbon double bonds (C = C) in a suitable position to undergo the photoreaction. The Ag(I) ion has proven to be reliable to generate photoactive materials based upon an ability of the metal to coordinate to pyridine rings and participate in argentophilic forces (Ag···Ag) [5]. Collectively, the noncovalent forces enable the C = C bonds to conform to the criteria of Schmidt to generate cyclobutane-based photoproducts upon UV-irradiation.

Herein, we report the integration of the 2-pyridyl group in the generation of a photoactive solid based on Ag(I) ions. Specifically, we demonstrate the ability of silver *p*-toluenesulfonate to form a photoactive complex with *trans*-1-(4-acetoxyphenyl)-2-(2-pyridyl)ethylene **1** that upon exposure to UV light generates the head-to-tail (ht) photoproduct *rctt*-1,3-bis(2-pyridyl)-2,4-bis(4-acetoxyphenyl)cyclobutane **2** in quantitative yield (Scheme 1). The extent of the photoreaction was confirmed by ^{1}H NMR spectroscopy and the stereochemistry of the photoproduct was confirmed by single-crystal X-ray diffraction (SCXRD).

2. Experimental

2.1. Materials

Trans-1-(4-acetoxyphenyl)-2-(2-pyridyl)ethylene **1** was prepared *via* a published report [6]. Silver *p*-toluenesulfonate ($\geq$ 99%) and ethanol (95%) were purchased from Sigma-Aldrich (St. Louis, MO) and used as received.

2.2. Methods

Photoreactions were conducted using a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. Single crystals were removed from the scintillation vial, finely ground using a mortar and pestle, and then placed between a pair of Pyrex glass plates. The samples were irradiated in 10-hour intervals. The overall yield of the photoreaction was monitored using ^{1}H NMR spectroscopy . ^{1}H NMR spectra were

Table 1. Crystallographic data for **1**, [Ag(*p*-tol)(**1**)$_2$]•(H_2O), and **2**.

Compound	1	[Ag(*p*-tol)(1)$_2$]•(H_2O)	2
CCDC code	1828456	1828457	1828458
Formula	$C_{15}H_{13}NO_2$	$C_{37}H_{35}AgN_2O_8S$	$C_{30}H_{26}N_2O_4$
Formula weight	239.28	775.60	478.53
Temperature	293(2)	293(2)	100(2)
Space group	*P2$_1$*	*P-1*	*P2$_1$/n*
a, Å	6.255(3)	9.6387(5)	9.9419(16)
b, Å	7.5546(7)	11.4673(6)	7.9044(12)
c, Å	13.6485(13)	16.7998(9)	15.922(2)
α, °	90	109.350(3)	90
β, °	102.349(17)	93.454(3)	106.760(4)
γ, °	90	92.031(3)	90
Volume, Å^3	630.0(3)	1745.78(16)	1198.1(3)
Z	2	2	2
Density (calculated), g/cm^3	1.261	1.475	1.326
μ, mm^{-1}	0.084	0.692	0.089
Scan	ω scans	ω and φ scans	ω and φ scans
θ range for data collection, °	3.06–25.34	1.288–26.460	2.171–26.013
Reflections measured	5609	30859	10384
Independent observed reflns.	2305	7108	2357
Independent reflns. [$I > 2\sigma$]	2008	5248	1606
Data / restraints / parameters	2305/1/165	7108/0/448	2357/0/164
R_{int}	0.0189	0.0329	0.0342
Final *R* indices [$I > 2\sigma$]	$R_1 = 0.0398$	$R_1 = 0.0361$	$R_1 = 0.0599$
	$wR2 = 0.0968$	$wR2 = 0.0934$	$wR2 = 0.1498$
R Indices (all data)	$R_1 = 0.0470$	$R_1 = 0.0562$	$R_1 = 0.0909$
	$wR2 = 0.1022$	$wR2 = 0.1079$	$wR2 = 0.1707$
Goodness-of-fit on F^2	1.079	1.080	1.049

collected using Bruker Fourier 300 and Avance-III 600 MHz spectrometers using DMSO-d_6 as the solvent.

2.3. Synthesis of bis(trans-1-(4-acetoxyphenyl)-2-(2-pyridyl)ethylene)silver(I) p-toluenesulfonate monohydrate [Ag(p-tol)(1)$_2$]•(H_2O)

The formation of [Ag(*p*-tol)(**1**)$_2$]•(H_2O) was achieved by dissolving **1** (50 mg, 0.209 mmol) in warm ethanol (2 mL) and then adding the solution to a solution of silver *p*-toluenesulfonate (29.2 mg, 0.104 mmol) in deionized water (2 mL). The vial was then covered in aluminum foil and the cap was securely fastened. Single colorless block crystals (36 mg, 0.046 mmol, 44% yield) suitable for X-ray diffraction formed within a period of 2 days.

2.4. Synthesis and purification of photoproduct rctt-1,3-bis(2-pyridyl)-2,4-bis(phenyl)cyclobutane 2

The formation of **2** was achieved in quantitative yield from [Ag(*p*-tol)(**1**)$_2$]•(H_2O) within 100 h of UV irradiation as determined by ^{1}H NMR spectroscopy. The cyclobutane **2** was isolated and purified by dissolving the photoreacted material in a 20 mL solution of water and methylene chloride (1:1 ratio). The organic layer was separated using a separatory funnel where two additional washings of 10 mL of methylene chloride were performed. Upon slow evaporation of the methylene chloride, small colorless block crystals of **2** suitable for single-crystal X-ray diffraction formed within a period of approximately 3 h (13 mg, 0.027 mmol, 59% yield after purification).

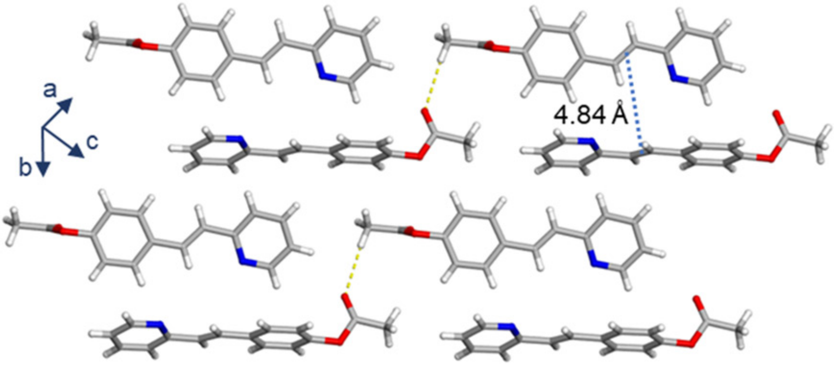


Figure 1. X-ray crystal structure of **1** illustrating both the C-H···O hydrogen bonds and the edge-to-face π-π stacking of aromatic rings.

2.5. Single-crystal and powder X-ray diffraction

Single crystals were secured to Mitegen magnetic mounts using Paratone oil. For all data sets, the reflection data were collected by means of a Bruker APEX II Kappa diffractometer using Mo K_α radiation ($\lambda = 0.71073$ Å). All diffraction data were collected at 290 K except for **2** which was collected at 100 K. Apex II was utilized to ensure maximum data redundancy, data collection, initial indexing, frame integration, Lorentz-polarization corrections, and final cell parameter calculations [7]. SADABS was employed to complete their multi-scan absorption corrections for all datasets [8]. The structures were solved using dual space methods and refined using difference Fourier techniques using SHELXT [9] and SHELXL [10], respectively, in the Olex2 graphical user interface [11]. The space groups were unambiguously verified using PLATON [12] after careful analysis of their systematic absences. Final structural refinements on all structures included anisotropic temperature factors on their non-hydrogen atoms. All hydrogen atoms were attached via the riding model at calculated positions using suitable HFIX commands. The crystallographic data for all structures are summarized in Table 1.

PXRD data were collected from samples mounted on glass slides by a Bruker D8 Avance X-ray diffractometer using $CuK\alpha_1$ radiation ($\lambda = 1.5418$ A˚) typically in the range of $5-35°$ two-theta (scan type: coupled TwoTheta/Theta; scan mode: continuous PSD fast; step size: 0.019°). The equipment was operated at 40 kV and 30 mA, and data was collected at room temperature. The phase of the bulk material was monitored throughout the photoreaction after each 10 h interval of UV irradiation (Figure S1).

3. Results and discussion

The majority of pyridine-based olefins studied using Ag(I) complexes have been based on the 4-pyridyl group [5, 13, 14], while the 3-pyridyl group has received considerably less attention [15–17]. The 4- and 3-pyridyl groups can be considered to be less sterically hindered owing to the positioning of the N-atom away from the central C = C

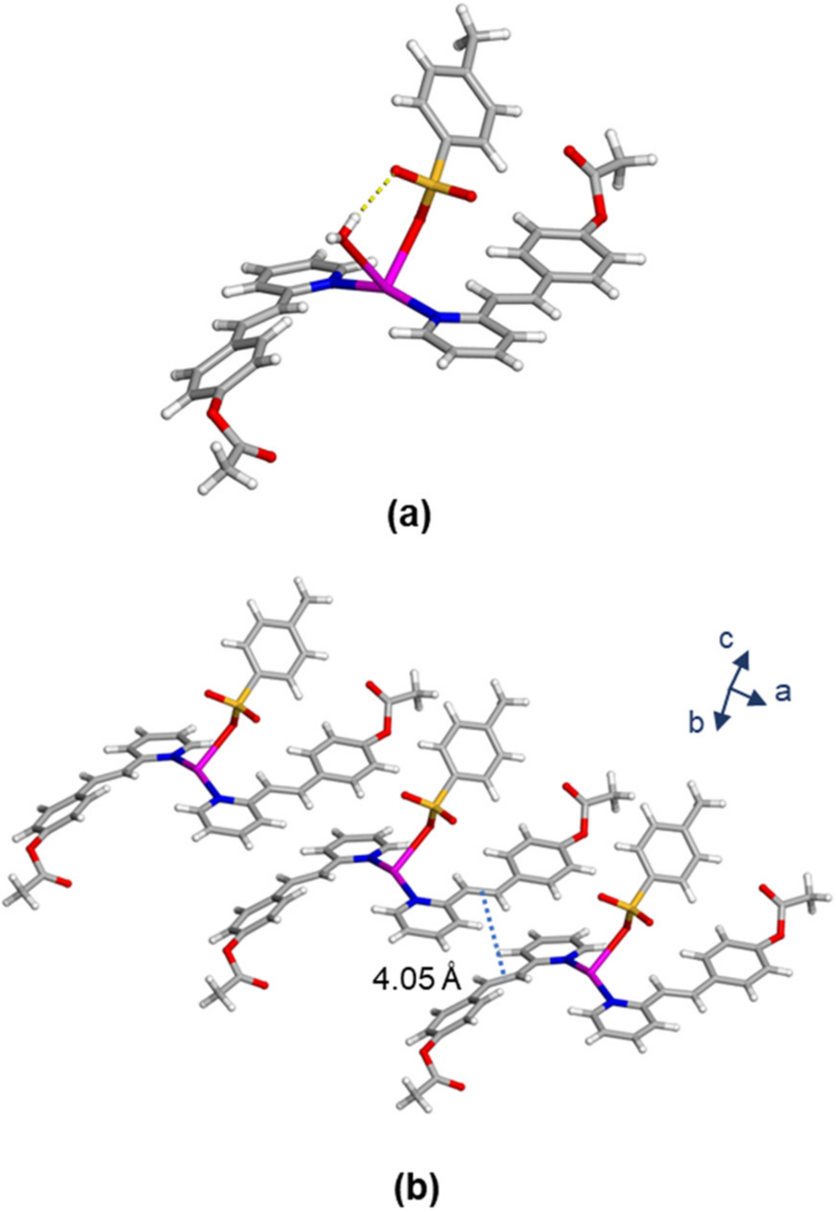


Figure 2. X-ray crystal structure of $[Ag(p\text{-tol})(\mathbf{1})_2]\bullet(H_2O)$ illustrating: (a) T-shaped coordination environment and (b) stacking of nearest-neighbor complexes that accounts for the ht photoproduct (water molecules were removed for clarity).

bond. Photoactive solids involving the 2-pyridyl group have involved organic co-crystals [18–22], salts [23–25], and a hydrate [26]. Four photoactive solids based on metal complexes with the 2-pyridyl group have been reported in the form $[Mn(SCN)_2(H_2O)_4]\bullet4(2,2'\text{-bpe})$, $[Mn(SCN)_2(H_2O)_2(2,4'\text{-bpe})_2]$, $(2,2'\text{-Hbpe})[Zn(NCS)_4]\bullet(H_2O)_2$ and $(2,2'\text{-Hbpe})(2,2'\text{-}H_2bpe)_{0.5}[Zn(NCS)_4]\bullet(H_2O)_2$ [27–29]. The 2-pyridyl group in each solid was not

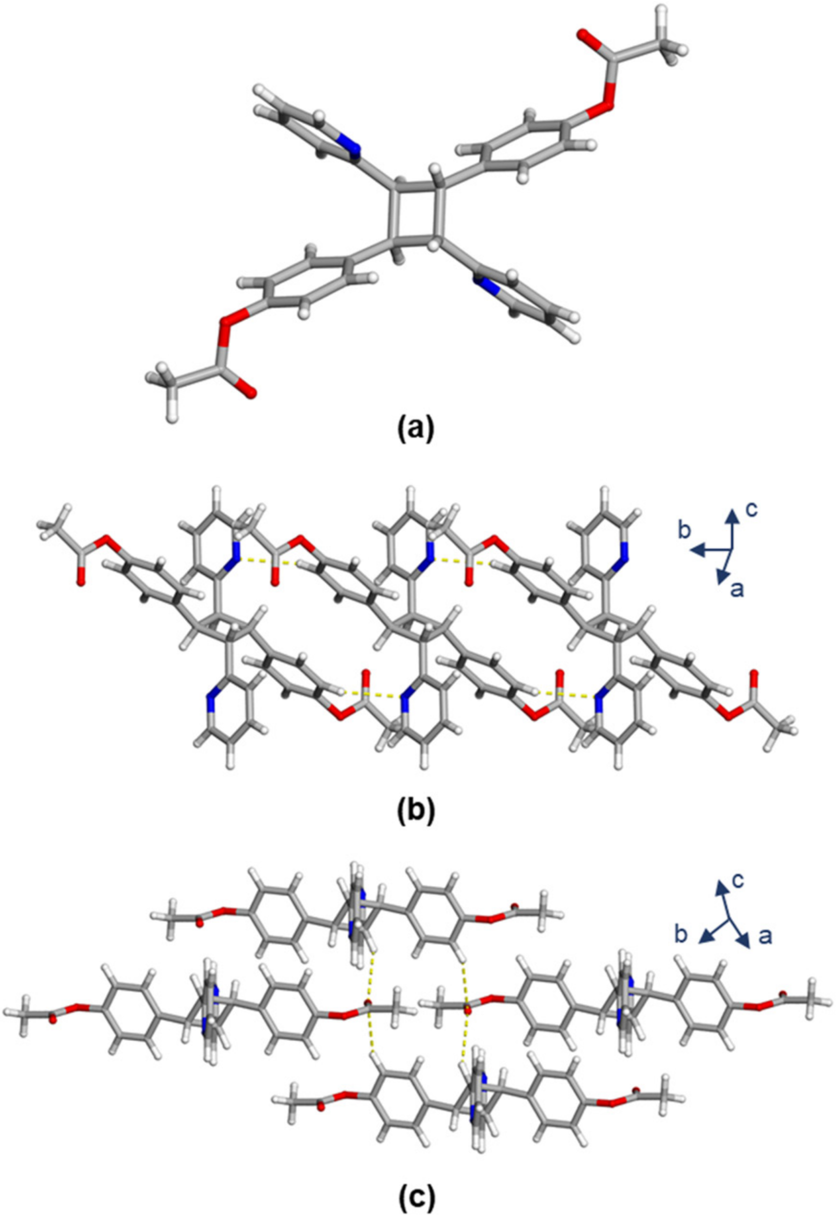


Figure 3. X-ray crystal structure of **2** illustrating: (a) ht-stereochemistry, (b) extended packing showing intermolecular C-H···N (b) and C–H···O and (c) hydrogen bonds.

coordinated to the metal center. In $[Mn(SCN)_2(H_2O)_4]\bullet 4(2,2'\text{-bpe})$, the 2-pyridyl groups interact with coordinated water molecules via O–H···N hydrogen bonds. In the $[Mn(SCN)_2(H_2O)_2(2,4'\text{-bpe})_2]$, the 4-pyridyl group is coordinated to the manganese metal atom while the 2-pyridyl group interacts with coordinated water molecules via O–H···N hydrogen bonds. Structures of $(2,2'\text{-}H_2bpe)[Zn(NCS)_4]\bullet(H_2O)_2$ and $(2,2'\text{-Hbpe})(2,2'\text{-}H2bpe)_{0.5}[Zn(NCS)_4]\bullet(H_2O)_2$ are sustained by interactions of pyridinium cations with water.

3.1. Pure solid 1

The olefin under investigation is photostable as a pure solid. The crystal structure of **1** reveals the alkene to crystallize in the chiral monoclinic space group $P2_1$ with a single molecule in the asymmetric unit. The aromatic rings are slightly twisted from co-planarity (rotation: 9.57°) while the acetoxy group lies nearly perpendicular to the phenyl ring (rotation: 88.60°) [30–32]. Neighboring molecules of **1** are approximately anti-parallel (rotation: 58.10°), participating in edge-to-face π-π forces (Figure 1). The carbonyl O-atom participates in a C–H···O hydrogen bond (C···O (Å): 3.560(4)) with a terminal methyl group. The 2-pyridyl groups point in the same direction in the solid, which accounts for the lack of inversion symmetry. Nearest-neighbor C = C bonds are separated by 4.84 Å, which is beyond the limit for photoreaction [33]. The photostability of **1** was confirmed from ^{1}H NMR spectroscopy by irradiating a sample placed between two Pyrex plates for a period of 50 h.

3.2. Photoactive Ag(I) complex

The components of [Ag(*p*-tol)(**1**)$_2$]•(H$_2$O) crystallize in the centrosymmetric triclinic space group *P-1*. Each Ag(I) atom is coordinated to two molecules of **1** (Ag···N (Å): 2.182(2) and 2.197(2)) and a single O-atom of the –SO$_3$ group (Ag···O (Å): 2.575(2)) giving a distorted T-shaped coordination environment (Figure 2(a)). A water molecule weakly coordinates with the Ag(I) ion (Ag···O (Å): 2.724(3)) and engages in two O–H···O hydrogen bonds to sulfonate ions (O···O (Å): 2.883(4) and 3.048(4)) within and between neighboring complexes. Similar to pure **1**, the acetoxy groups are twisted from the plane of the phenyl rings (rotation: 47.85° or 69.95°).

The Ag(I) complexes pack to engage in π-π interactions running along the crystallographic *a*-axis. The stacking supports the coordinated alkenes to assume a face-to-face and head-to-tail geometry such that nearest-neighbor C = C bonds are parallel and separated by 4.05 Å (Figure 2(b)). The stacked geometry conforms to the geometry of Schmidt for a photodimerization in a solid.

When a powdered crystalline sample of [Ag(*p*-tol)(**1**)$_2$]•(H$_2$O) was irradiated using broadband UV light (450 W medium pressure Hg-lamp) the alkene reacted to form **2** in quantitative yield. The formation of **2** was evidenced in the ^{1}H NMR spectrum of the photoreacted material by the disappearance of the resonances of the olefinic protons centered at 7.30 and 7.66 ppm and the appearance of cyclobutane peaks at 4.65 and 4.85 ppm (Figure S5). A large mutual spin-spin coupling constant of 16.1 Hz indicated an anti-orientation, while COSY correlation peaks between and well-resolved HSQC correlations further supported the assignment of olefinic protons (Figure S6). The identity of the photoproduct **2** was, thus, confirmed by a battery of two-dimensional ^{1}H-^{1}H homonuclear and ^{1}H-^{13}C heteronuclear NMR experiments of the photoreacted material (Figure S7). We note that PXRD diffractograms during the course of the photoreaction revealed the solid to retain crystallinity while undergoing a change in phase (Figure S1).

3.3. Stereochemistry of photoproduct 2

The stereochemistry of **2** was confirmed by SCXRD (Figure 3(a)). The photoproduct **2** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$, with a half of a molecule in the asymmetric unit. The molecule sits around a center of inversion. Each acetoxy group is, similar to the parent alkene **1**, twisted nearly perpendicular to each phenyl ring (rotation: 85.39°). C–H···N hydrogen bonds (C···N (Å): 3.444(3)) form between the pyridyl N-atom and phenyl ring to generate a 1D array along the crystallographic *b*-axis (Figure 3(b)). The carbonyl O-atoms participate in C–H···O hydrogen bonds with H-atoms on the phenyl (C···O (Å): 3.456(3)) and cyclobutane (C···O (Å): 3.565(3)) rings to form 2D sheets in the crystallographic *ab* plane (Figure 3(c)).

4. Conclusion

In this report, we have described a solid-state photodimerization to be supported by coordination between Ag(I) and 2-pyridyl groups. The photoreaction involved stacked metal complexes. We are currently investigating additional Ag(I) salts involving 2-pyridyl that afford access to photoactive solids.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

R.H.G. gratefully acknowledges financial support from Webster University in the form of both Faculty Research Grants and Faculty Development Fund. L.R.M. gratefully acknowledges the National Science Foundation [DMR-1708673] for funding. G.C.-A. gratefully acknowledges CONACYT-COVEICYDET and the University of Iowa Graduate College for funding.

References

[1] L.R. MacGillivray, G.S. Papaefstathiou, T. Friščić, T.D. Hamilton, D.-K. Bučar, Q. Chu, D.B. Varshney, I.G. Georgiev. *Acc. Chem. Res.*, **41**, 280 (2008).
[2] M.-M. Gan, J.-G. Yu, Y.-Y. Wang, Y.-F. Han. *Cryst. Growth. Des.* **18**, 553 (2018).
[3] S. Poplata, A. Tröster, Y.-Q. Zou, T. Bach. *Chem. Rev*., **116**, 9748 (2016).
[4] R. Medishetty, I.-H. Park, S.S. Lee, J.J. Vittal. *Chem. Commun*., **52**, 3989 (2016).
[5] Q. Chu, D.C. Swenson, L.R. MacGillivray. *Angew. Chem*., **117**, 3635 (2005).
[6] H.-J. Choi, M.-G. Song, Y.-H. Sim, H.-K. Bae, J.-W. Kim, L.S. Park. *Mol. Cryst. Liq. Cryst*., **531**, 47 (2010).
[7] *Bruker AXS Inc, Madison, WI* (2005).
[8] L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. Stalke. *J. Appl. Crystallogr*., **48**, 3 (2015).
[9] G.M. Sheldrick. *Acta. Cryst*., **D65**, 148 (2009).
[10] G.M. Sheldrick. *Acta Cryst. C*, **71**, 3 (2015).
[11] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A. Howard, H. Puschmann. *J. Appl. Crystallogr*., **42**, 339 (2009).
[12] A. Spek. *Acta Crystallogr., Sect. A*, **46**, c34 (1990).
[13] C.Y. Chen, J.Y. Zeng, H.M. Lee. *Inorg. Chim. Acta*, **360**, 21 (2007).
[14] R. Medishetty, S.C. Sahoo, C.E. Mulijanto, P. Naumov, J.J. Vittal. *Chem. Mater*., **27**, 1821 (2015).
[15] M. Garai, K. Biradha. *Chem. Eur. J*., **23**, 273 (2017).
[16] A. Gordillo, M.A. Ortuño, C. López-Mardomingo, A. Lledós, G. Ujaque, E. de Jesús. *J. Am. Chem. Soc*., **135**, 13749 (2013).
[17] S. Florio, L. Troisi. *J. Org. Chem*. **61**, 4148 (1996).

[18] G.S. Papaefstathiou, A.J. Kipp, L.R. MacGillivray. *Chem. Commun*., 2462 (2001).

[19] G.S. Papaefstathiou, A.J.E. Duncan, L.R. MacGillivray. *Chem. Commun.* **50**, 15960 (2014).

[20] T.D. Hamilton, G.S. Papaefstathiou, L.R. MacGillivray. *CrystEngComm*, **4**, 223 (2002).

[21] A.J. Duncan, R.L. Dudovitz, S.J. Dudovitz, J. Stojaković, S.S. Mariappan, L.R. MacGillivray. *Chem. Commun*., **52**, 13109 (2016).

[22] B.R. Bhogala, B. Captain, A. Parthasarathy, V. Ramamurthy. *J. Am. Chem. Soc*., **132**, 13434 (2010).

[23] Y. Hill, M. Linares, A. Briceño. *New J. Chem*., **36**, 554 (2012).

[24] S. Chantrapromma, K. Chanawanno, N. Boonnak, H.-K. Fun. *Acta Crystallogr., Sect. E*, **70**, o510 (2014).

[25] G.K. Kole, U. Sambasivam, G.K. Tan, J.J. Vittal. *Cryst. Growth Des*., **17**, 2694 (2017).

[26] G.S. Papaefstathiou, T. Friščić, L.R. MacGillivray. *J. Supramol. Chem*., **2**, 227 (2002).

[27] A. Briceño, D. Leal, R. Atencio, G. Díaz de Delgado. *Chem. Commun*., 3534 (2006).

[28] Y. Hill, A. Briceño. *Chem. Commun*., 3930 (2007).

[29] A. Briceño, Y. Hill. *Acta Crystallogr. Sect. E Struct. Rep. Online* , **14**, 6121 (2012).

[30] P.-Q. Huang, Y.-H. Huang, H. Geng, J.-L. Ye. *Sci. Rep*., **6**, 28801 (2016).

[31] R. Datta, V. Ramya, M. Sithambaresan, M.R.P. Kurup. *Acta Crystallogr., Sect. E*, **69**, 1549 (2013).

[32] S. Ritter, J.-M. Neudorfl, J. Velder, H.-G. Schmalz. *Acta Crystallogr., Sect. E*, **65**, 2229 (2009).

[33] G. Schmidt. *Pure Appl. Chem*., **27**, 647 (1971).