

Anion-Templated Self-Assembly of Silver(I) Frameworks Bridged by μ -, μ_3 -, μ_4 -1,2,4,5-Tetrazine

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The formation of Ag(I)-1,2,4,5-tetrazines(ttz) based coordination polymers via the Ag–N coordination and anion– π interactions is described. Coordination-driven self-assembly is a key step to construct coordination polymers, and ttz, an electron-deficient aromatic ring compound, forms interesting anion– π interactions. In this study, a series of silver salts, AgX [X = BF₄, PF₆ and CF₃SO₃ (OTf)], is introduced to determine the influence of shape and size of anions on the formation of coordination polymers, {[Ag(ttz)](BF₄)}_n (**1**), {[Ag₂(ttz)₃](PF₆)₂}]_n (**2**) and {[Ag₂(ttz)₃(OTf)](OTf)}_n (**3**). It shows different types of channels in polymers and the coordination modes of ttz (μ , μ_3 , and μ_4). The structure of coordination polymers and the influence of anion– π interactions are revealed by single crystal X-ray diffraction. In particular, **3** shows not only the anion– π interaction but also the coordination between the anion and Ag(I) which contributes to the unique framework compared to **1** and **2**.

Keywords: Anion– π interactions, Coordination polymer, Tetrazine, Anion templating effect, Silver complex

Introduction

Coordination-driven self-assembly, which is closely concerned with the coordination preference of metal centers and directionality of multitopic bridging ligands, is considered a key process in the construction of coordination supramolecular architectures.^{1–7} During the assembly processes, noncovalent interactions such as hydrogen bonding, and π – π , cation– π , and anion– π interactions play a crucial role in organizing the resulting supramolecular coordination assemblies.^{8–10}

Especially, anion– π interactions, attractive forces between anions and electron-deficient aromatic rings, have been increasingly used to design functional supramolecular materials with promising applications for colorimetric sensors and hosts for selective anion recognition and anion carriers.^{11–21} Among the π –acidic aromatic rings, the coordination chemistry of 1,2,4,5-tetrazines (ttz), which are N-heteroaromatic rings composed of four nitrogen and two carbon atoms, has attracted great attention because of their π -electron deficiency and coordination affinity as multiple N-donor ligands with strong π -back bonding ability from lowly occupied π^* orbitals.²²

A number of quantum chemical and crystallographic studies have been carried out to understand the nature of the anion– π interaction between 1,2,4,5-tetrazines and

anions.^{23–26} In addition to these efforts, Dunbar *et al.* emphasized the importance of anion– π interactions as a driving force to stabilize supramolecular architectures of discrete Fe(II) metallacycles, where the use of different size of anions lead to the formation of different structures of Fe(II) complexes via anion– π interaction between π -acidic 1,2,4,5-tetrazine rings and the anions.²⁷ Despite these successful examples, the adoption of anion– π interactions as directing elements in more complex supramolecular systems, such as coordination polymers and frameworks, remains challenging because each subunit can affect neighboring units and multiple types of systems such as coordination modes of ligands or metal ions, which leads to the formation of unexpected coordination topologies or structures. To understand the effect of anion– π interaction in the multicomponent self-assembly, d¹⁰ metal cations were widely used with various anions to result architectural diversity in molecules or polymers. For that, Wu's group reported anion directed Ag(I) complexes and its properties depending on the different anions, and Domasevitch's group reported the formation of anion directed coordination polymers consisting of Ag(I) or Cu(I) and N-heteroaromatic rings derivatives with various anions.^{28–30}

For this purpose, we reported Ag(I)-3,6-dimethoxy-1,2,4,5-tetrazine (dmotz) coordination polymers, where anion π -interaction between the π -acidic dmotz ring and

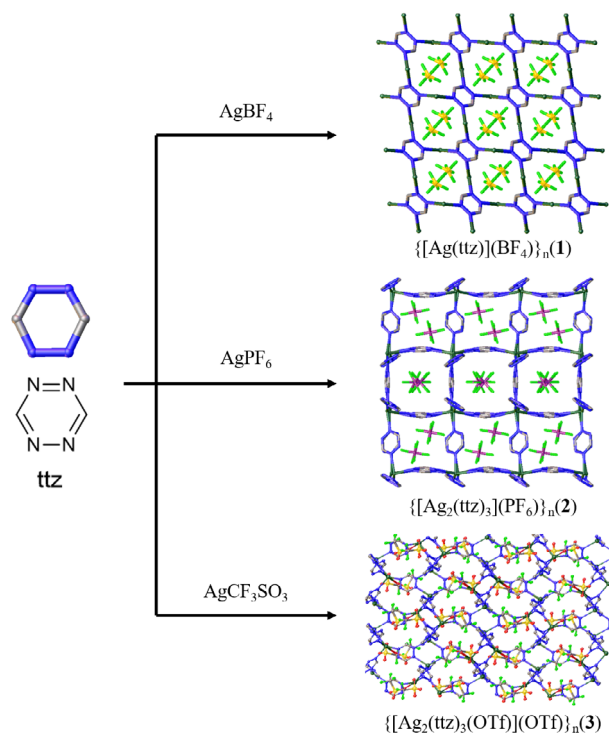
CF_3SO_3^- (OTf^-) and ClO_4^- guided the formation of the 1D coordination polymer $[\text{Ag}(\text{dmotz})(\text{OTf})]_n$ and the 2D grid polymer $\{[\text{Ag}(\text{dmotz})_2](\text{ClO}_4)]_n$, respectively. The structures underwent irreversible conversion from $[\text{Ag}(\text{dmotz})(\text{OTf})]_n$ to $\{[\text{Ag}(\text{dmotz})_2](\text{ClO}_4)]_n$ in the presence of an equivalent of ClO_4^- .³¹

As a part of our aim for better understanding the role of anion- π interactions in the formation of coordination polymers, we have synthesized coordination polymers using more concise ligand, ttz, and various AgX ($\text{X} = \text{BF}_4$, PF_6 and OTf) salts. Herein, we report the anion-directed assembly of Ag(I) -ttz coordination polymers $\{[\text{Ag}(\text{ttz})](\text{BF}_4)]_n$ (**1**), $\{[\text{Ag}_2(\text{ttz})_3](\text{PF}_6)_2]_n$ (**2**) and $\{[\text{Ag}_2(\text{ttz})_3](\text{OTf})(\text{OTf})]_n$ (**3**), and their structural characteristics, including anion- π interactions.

Results and Discussion

Treatment of ttz ligand and Ag(I) salts with various counteranions (BF_4^- , PF_6^- or OTf^-) in organic solvent (dichloromethane [DCM] or tetrahydrofuran [THF]) at room temperature leads to the formation of dark-red crystalline products. The single-crystal X-ray diffraction analysis of compounds **1–3** reveals three-dimensional (3D) coordination polymeric frameworks, resulting from the arrangement of silver ions and ttz ligands mediated by different anions (Scheme 1).

Compound **1** crystallizes in orthorhombic space group $Im2a$ with $Z = 2$ (Supporting Information Table S1) and



Scheme 1. Synthesis and structures of silver-tetrazine coordination frameworks **1**, **2**, and **3**.

the asymmetric unit of **1** is composed of one Ag(I) ion and half of the ttz ligand. The BF_4^- anion, which is accommodated in the channel of **1**, is disordered over three positions which has 2:2:1 occupancy ratio, where allowing anion- π interactions with ttz. Each silver ion, which adopts a distorted square planar geometry, is bound to four tetrazine-N donors in four ttz ligands (Figure 1(a)). The 4-coordinate index, τ_4 for **1** is $[360 - (179.32 + 179.32)]/141 = 0.01$, which is close to zero for a square planar.³² The Ag-N bond distances and N-Ag-N bond angles vary between 2.461 (7)–2.488 (7) Å and 86.7 (4), and 93.0 (4)°, respectively (Figure 1(b)). Bond distances and angles are in good agreement with the corresponding data from the literature (2.4242(18)–2.4857(19) Å and 85.59(6), 97.47(9)°).²⁹ Each ttz ligand, which displays a μ_4 -coordination, binds to four Ag(I) atoms, with the 1,4-positioned $\text{Ag}\cdots\text{Ag}$ separation distance of 7.6389(2) Å. The coordination-driven assembly of μ_4 -coordinated ttz ligands and Ag(I) ions results in a 3D coordination framework in a rectangular shape (Figure 1(d)).

Notably, **1** exhibits one-dimensional rhombic channels with an average cross-sectional distance of 8.988 Å along the crystallographic bc plane (Figure 1(d)), which can provide accommodation of the BF_4^- anions. Among BF_4^- disordered models, the highest occupied model of BF_4^- anion is illustrated and noncovalent contacts are found between a BF_4^- anion and surrounding ttz ligands in the structure of **1** (Figure 1(c)). The distances between the closest F atoms and the centroid of the neighboring tetrazine ring in **1** are 2.774 (10) Å, and the closest distance of $\text{F}\cdots\text{C}_{\text{ttz}}$ is 2.884 (11) Å which is shorter than the total van der Waals radius of following atoms, $\Sigma R_{\text{vdW}} \text{F}\cdots\text{C} = 3.17$ Å and $\Sigma R_{\text{vdW}} \text{F}\cdots\text{N} = 3.25$ Å.³³

It has been reported that the geometry of accommodated anions has a strong impact on the resulting coordination structures constructed from a given metal and ligands.^{30,34,35} Therefore, the variation of anions with different molecular geometries is expected to alter the structure of the obtained frameworks. In addition, PF_6^- was used as an anion to construct a different structure of a coordination framework compared to **1**. Powder X-ray diffraction (PXRD) of **1** is in agreement with the simulated pattern from SC-XRD data (Supporting Information Figure S1), and TGA curve of **1** shows that it begins to decompose at 220°C (Supporting Information Figure S4).

X-ray crystallography analysis of **2** reveals that it crystallizes in orthorhombic space group $Pnma$ with $Z = 8$ (Supporting Information Table S1) and the asymmetric unit is composed of two crystallographically independent Ag(I) ions and three and a half ttz ligands. One of PF_6^- , which is accommodated in the channel of **2**, is disordered between two positions in 1:1 ratio, allowing interactions to ttz in a short anion- π distance.

As shown in Figure 2(a), the Ag(I) complex exhibits a distorted trigonal bipyramidal geometry by coordinating with five N atoms of five ttz ligands. The 5-coordinate

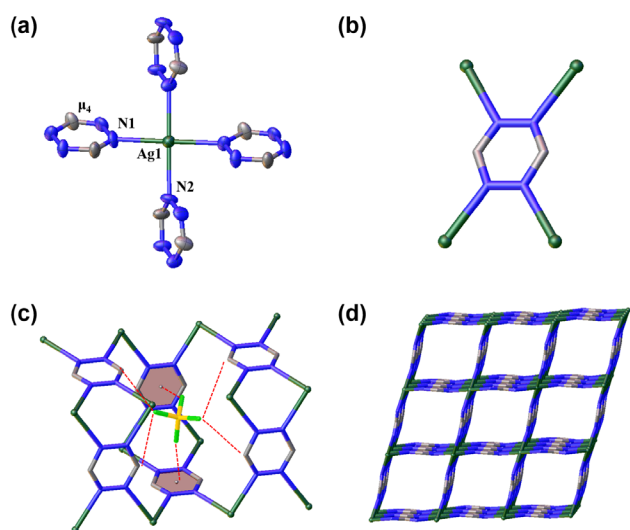


Figure 1. (a) Distorted square planar geometry of Ag(I) with ttz in **1**; (b) μ_4 -coordination mode of ttz; (c) the anion- π interaction between BF_4^- and ttz ligands; (d) view of the coordination framework in **1** without anions. (Hydrogen atoms have been omitted for clarity. Gray = carbon, blue = nitrogen, dark green = silver, yellow = boron, green = fluorine).

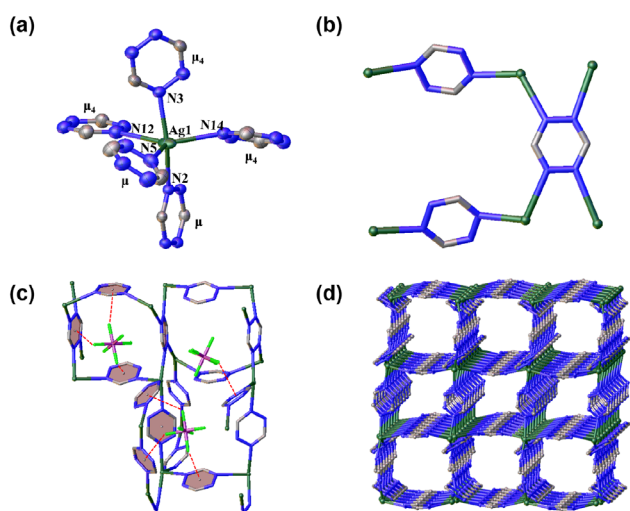


Figure 2. (a) Distorted trigonal bipyramidal geometry of Ag(I) with ttz in **2**; (b) μ , μ_4 -coordination modes of ttz; (c) the anion- π interaction between PF_6^- and ttz ligands; (d) view of the coordination framework in **2** without anions. (Hydrogen atoms have been omitted for clarity. Gray = carbon, blue = nitrogen, dark green = silver, purple = phosphorus, green = fluorine).

index, τ_5 , represents a perfect trigonal bipyramidal when τ_5 is close to 1, and square pyramidal when it is close to 0. For **2**, τ_5 is $(165.50-130.10)/60 = 0.6$, and $(159.8-129.0)/60 = 0.51$ for each Ag(I) atoms, which mean a distorted geometry between trigonal bipyramidal and square pyramidal.³⁰ The average Ag–N bond distances are 2.430(12) Å and 2.413(12) Å, which is shorter than those in **1**. As seen from Figure 2(b), ttz ligands in **2** show μ_4 - and

μ -coordination modes. While the former is almost identical to that of **1**, at the 1,4-positioned Ag atoms for ttz, Ag...Ag separation distance of 7.3609(4) Å, the latter, in which the two tetrazine-N donors occupy the two peripheral points on the tetrazine ring and are bound to two Ag(I) ions, is not observed in the framework of **1**. The Ag...Ag separation distance caused by the μ -coordination mode is 7.2076(4) Å in average. Octahedral geometry and bulkier size of PF_6^- than BF_4^- would strongly influence the coordination-driven assembly of Ag(I) ions and ttz ligands, and cause the distinct coordination modes of ttz ligands. In addition, the framework is afforded and it shows two types of channels along the crystallographic *ab* plane with the average cross-sectional distances at 9.529(4) Å and 10.193(4) Å due to the accommodation of PF_6^- (Figure 2(d)).

As shown in Scheme 1, PF_6^- are placed in different positions according to the shape of channels. Among PF_6^- disordered model, the highest occupancy is illustrated and the anion- π interactions between PF_6^- anions and ttz ligands are observed in **2** (Figure 2(c)). Specifically, four F atoms from a PF_6^- anion interact with four neighboring tetrazine rings: two μ_4 - and two μ -ttz ligands. The closest distance between F atoms and the centroid of ttz ligands in **2** are 2.711(15) Å, 2.825(15) Å, and 2.986(13) Å. Powder X-ray diffraction (PXRD) of **2** is in agreement with the simulated pattern (Supporting Information Figure S2), and TGA curve of **2** shows that it begins to decompose at 100°C (Supporting Information Figure S4).

The frameworks of **1** and **2** show the different coordination and channels depending on the size of anions and the characteristics of anion- π interactions. Since the two anions, BF_4^- and PF_6^- , do not form coordination bonds, we decided to introduce another anion that readily coordinates to Ag to investigate whether the anion forms coordinative and/or anion- π interactions. Therefore, we attempted to isolate a coordination polymer from the reaction of the ttz ligand and Ag(I) salts in the presence of OTf^- . The O atoms in OTf^- have been reported to be capable of coordinating to metal centers in coordination frameworks.²⁹

Compound **3** crystallizes in monoclinic space group of *P2₁/n* with *Z* = 4 (Supporting Information Table S1). The asymmetric unit of **3** is composed of three ttz ligands bridged by Ag(I) ions, and two different interaction modes of OTf^- , anion- π interaction with ttz and coordination of O atom to Ag(I), are found. The Ag(I) ion adopts a distorted trigonal bipyramidal geometry, and each Ag(I) ion is coordinated by four tetrazine-N donors from four ttz ligands and one oxygen atom in OTf^- . The 5-coordinate index, τ_5 , for **3** is 0.4 which shows a highly distorted geometry between trigonal bipyramidal and square pyramidal, which is in accordance with a crystal data.³² The average Ag–N bond distances are 2.447(2) Å and 2.439(2) Å for each Ag atoms, and a coordinated Ag–O distance is 2.562(2) Å. Unlike **1** and **2**, ttz in **3** shows μ - and μ_3 -coordination modes (Figure 3(b)). Moreover, two types of μ -coordination modes are coexist in **3**, where the Ag(I) atoms are coordinated to ttz at the 1,4- or 1,5-position,

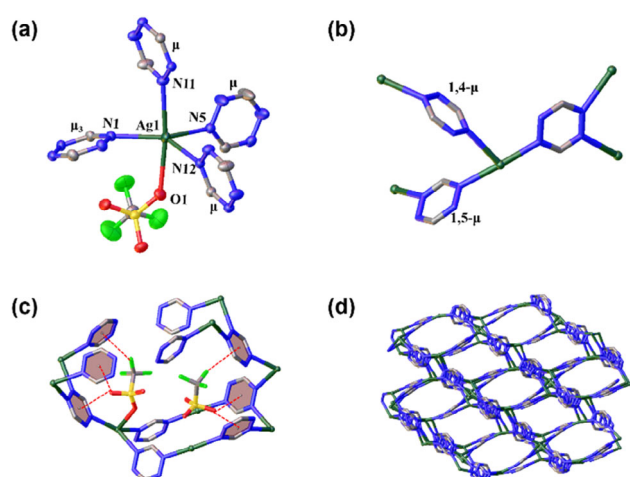


Figure 3. (a) Distorted square pyramidal geometry of Ag(I) with ttz in **3**; (b) μ , μ_3 -coordination modes of ttz; (c) the anion- π interaction between OTf⁻ and ttz ligands; (d) view of the coordination framework in **3** without anions. (Hydrogen atoms have been omitted for clarity. Gray = carbon, blue = nitrogen, dark green = silver, red = oxygen, yellow = sulfur, green = fluorine).

and it accounts for a unique framework structure in **3** (Figure 3(d)) in comparison to **1** and **2**. Because of the interaction between OTf⁻ and ttz and the multiple coordination modes of ttz, oval-shaped channels are formed to accommodate anions. In detail, both O and F atoms in OTf⁻ participate in anion- π interactions with the surrounding ttz ligands with average distances of 3.071(3) Å and 3.264(3) Å, respectively. Powder X-ray diffraction (PXRD) of **3** is in agreement with the simulated pattern (Supporting Information Figure S3), and TGA curve of **3** shows that it begins to decompose at 200 °C (Supporting Information Figure S4).

Conclusion

In summary, we have reported a series of Ag(I) and ttz-based coordination frameworks containing anions that were driven by Ag-N coordination and anion- π interactions. Single crystal X-ray diffraction analysis revealed that the distinct framework was constructed depending on the coordination mode of the N-donor ligand and anion template effect. The bond distances of Ag-N in **1**, **2**, and **3** were similar, but different types of channels were formed due to the various coordination environments of Ag ions and the various coordination modes of ttz ligands. Through the crystal structural analysis of each framework, we demonstrated that anion- π interactions as well as metal coordination play a key role in forming self-assembled structures.

Experimental

General. The ligand ttz was synthesized by a modification of literature methods.³⁰ Other chemicals were purchased from commercial sources and used without further purification. Silver(I)

tetrafluoroborate (AgBF₄, 99%, Alfa Aesar), silver(I) hexafluorophosphate (AgPF₆, 98%, Alfa Aesar), and silver(I) trifluorotrimethanesulfonate (AgOTf, 98%, Alfa Aesar) were used as received. The FT-IR spectra were recorded with a Vertex 70 FT-IR spectrometer. Synthesized complexes are characterized by single crystal X-ray determination and elemental analysis. Single crystal X-ray analysis was performed on a Bruker AXS D8 Venture. Elemental analysis (EA) data were obtained from the Organic Chemistry Research Center at Sogang University. PXRD patterns were obtained using a Rigaku Ultima IV apparatus equipped with a graphite-monochromated Cu $\kappa\alpha$ radiation source (40 kV, 40 mA). Thermogravimetric analysis (TGA) measurements were conducted using a Shimadzu TGA-50 under a nitrogen atmosphere at a heating rate of 10 °C/min. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-1885056(1), 1885057(2), 1885058(3)).

Synthesis of {[Ag(ttz)](BF₄)}_n (1**).** A solution of ttz (20 mg, 0.24 mmol) in dichloromethane (DCM) (5 mL) was added dropwise to a solution of AgBF₄ (23 mg, 0.12 mmol) in dichloromethane (15 mL). The reaction vessel was shielded from light and the solution was stirred for 2 h at room temperature. After stirring, the solvent was removed under reduced pressure. The resulting purple crystalline precipitate was washed with dichloromethane. The purple powder was dried *in vacuo*. Yield: 12 mg, 42%. Crystals which have suitable quality to SC-XRD were obtained by a liquid-liquid diffusion of pentane to DCM solution at low temperature. Anal. Calcd for C₂H₂AgBF₄N₄: C, 8.68; H, 0.73; N, 20.25. Found: C, 8.62; H, 0.79; N, 20.47.

Synthesis of {[Ag₂(ttz)₃](PF₆)₂)}_n (2**).** A solution of ttz (14 mg, 0.17 mmol) in THF (5 mL) was added dropwise to a solution of AgPF₆ (28 mg, 0.11 mmol) in THF (10 mL). The reaction vessel was shielded from light and the solution was stirred for 2 h at room temperature. After stirring, the solvent was removed under reduced pressure. The resulting orange crystalline precipitate was washed with dichloromethane. The orange powder was dried *in vacuo*. Yield: 12 mg, 31%. Crystals that have suitable quality to SC-XRD were obtained by a liquid-liquid diffusion of pentane to THF solution at low temperature. Anal. Calcd for C₇H₈Ag₂P₂F₁₂N₁₄: C, 10.59; H, 1.02; N, 24.70. Found: C, 10.67; H, 1.09; N, 23.95.

Synthesis of {[Ag₂(ttz)₃](OTf)(OTf)}_n (3**).** A solution of ttz (31 mg, 0.38 mmol) in THF (5 mL) was added dropwise to a solution of AgOTf (48 mg, 0.19 mmol) in THF (5 mL). The reaction vessel was shielded from light and the solution was stirred for 2 h at room temperature. After stirring, the solvent was removed under reduced pressure. The resulting dark orange crystalline precipitate was washed with dichloromethane. The dark orange powder was dried *in vacuo*. Yield: 73 mg, 80%. Crystals that have suitable quality to SC-XRD were obtained by a liquid-liquid diffusion of pentane to THF solution at low temperature. Anal.

Calcd for $C_8H_6Ag_2F_6N_{12}O_6S_2$: C, 12.64; H, 0.80; N, 22.11. Found: C, 12.79; H, 0.72; N, 22.09.

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Conflict of interest. The authors declare no conflict of interest.

Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

References

1. C. Janiak, *Dalton Trans* **2003**, 2781.
2. S. L. James, *Chem. Soc. Rev.* **2003**, 32, 276.
3. M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, A. Wachter, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2002**, 99, 4900.
4. S. Surblé, F. Millange, C. Serre, T. Düren, M. Latroche, S. Bourrelly, P. L. Llewellyn, G. Férey, *J. Am. Chem. Soc.* **2006**, 128, 14889.
5. D. MasPOCH, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.* **2004**, 14, 2713.
6. H. Shin, S. Oh, H. Jun, M. Oh, *Bull. Kor. Chem. Soc.* **2020**.
7. S. Hong, Y. Kim, Y. Kim, K. Suh, M. Yoon, K. Kim, *Bull. Kor. Chem. Soc.* **2020**.
8. J. Ćezáć, P. Hobza, *Chem. Rev.* **2016**, 116, 5038.
9. D. P. Malenov, G. V. Janjić, V. B. Medaković, M. B. Hall, S. D. Zarić, *Coord. Chem. Rev.* **2017**, 345, 318.
10. P. Molina, F. Zapata, A. Caballero, *Chem. Rev.* **2017**, 117, 9907.
11. M. Savastano, C. Bazzicalupi, C. Garcia, C. Gellini, M. D. López de la Torre, P. Mariani, F. Pichierri, A. Bianchi, M. Melguizo, *Dalton Trans.* **2017**, 46, 4518.
12. J.-Z. Liao, X.-J. Dui, H.-L. Zhang, X.-Y. Wu, C.-Z. Lu, *CrystEngComm* **2014**, 16, 10530.
13. J. Wang, X. Gu, P. Zhang, X. Huang, X. Zheng, M. Chen, H. Feng, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *J. Am. Chem. Soc.* **2017**, 139, 16974.
14. J.-Z. Liao, X.-Y. Wu, J.-P. Yong, H.-L. Zhang, W.-B. Yang, R. Yu, C.-Z. Lu, *Cryst. Growth Des.* **2015**, 15, 4952.
15. S. P. Mahanta, B. S. Kumar, S. Baskaran, C. Sivasankar, P. K. Panda, *Org. Lett.* **2012**, 14, 548.
16. J. Zhao, G. Li, C. Wang, W. Chen, S. C. J. Loo, Q. Zhang, *RSC Adv.* **2013**, 3, 9653.
17. S. Guha, S. Saha, *J. Am. Chem. Soc.* **2010**, 132, 17674.
18. A. Kim, R. Ali, S. H. Park, Y.-H. Kim, J. S. Park, *Chem. Commun.* **2016**, 52, 11139.
19. M. Giese, M. Albrecht, A. Valkonen, K. Rissanen, *Eur. J. Org. Chem.* **2013**, 2013, 3247.
20. S. Banerjee, P. Dastidar, *CrystEngComm* **2013**, 15, 9415.
21. C.-Y. Wang, J.-F. Zou, Z.-J. Zheng, W.-S. Huang, L. Li, L.-W. Xu, *RSC Adv.* **2014**, 4, 54256.
22. W. Kaim, *Coord. Chem. Rev.* **2002**, 230, 127.
23. B. L. Schottel, H. T. Chifotides, K. R. Dunbar, *Coord. Chem. Rev.* **2008**, 37, 68.
24. A. K. Rappé, E. R. Bernstein, *J. Phys. Chem. A* **2000**, 104, 6117.
25. A. Hesselmann, G. Jansen, M. Schütz, *J. Am. Chem. Soc.* **2006**, 128, 11730.
26. M. Piacenza, S. Grimme, *ChemPhysChem* **2005**, 6, 1554.
27. H. T. Chifotides, I. D. Giles, K. R. Dunbar, *J. Am. Chem. Soc.* **2013**, 135, 3039.
28. H. Wu, L. Xia, Y. Qu, K. Zhao, C. Wang, Y. Wu, *Appl. Organomet. Chem* **2020**, 34, 2.
29. I. A. Gural'skiy, D. Escudero, A. Frontera, P. V. Solntsev, E. B. Rusanov, A. N. Chernega, H. Krautscheid, K. V. Domasevitch, *Dalton Trans.* **2009**, 2856.
30. A. S. Degtyarenko, P. V. Solntsev, H. K. Krautscheid, E. B. Rusanov, A. N. Chernega, K. V. Domasevitch, *New J. Chem.* **2008**, 32, 1910.
31. P. Kang, S. Jung, J. Lee, H. J. Kang, H. Lee, M.-G. Choi, *Dalton Trans.* **2016**, 45, 11949.
32. L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans* **2007**, 955.
33. M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, 113, 5806.
34. M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2327.
35. X.-P. Zhou, X. Zhang, S.-H. Lin, D. Li, *Cryst. Growth Des.* **2007**, 7, 485.