

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard [Terms & Conditions](#) and the [ethical guidelines](#) that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

Multi-nuclear silver(I) and copper(I) complexes: novel bonding mode for bispyridylpyrrolides

Xiao-Hui Hu, Yan Liang, Chen Li, Xiao-Yi Yi,*

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

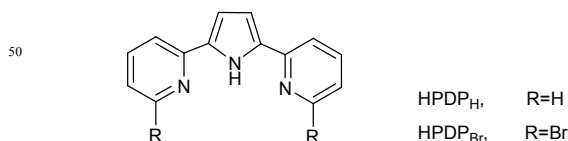
First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

Reaction of deprotonated 2,5-bis(2'-pyridyl)pyrrole (HPDP_H) with AgOTf (where OTf = triflate) in THF readily yields yellow triangular Ag₃ complex [(PDP_H)Ag]₃ (**1**), of which av. Ag...Ag distance is 2.902 Å. A mixture of HPDP_H and AgOTf reacts with PPh₃ to afford linear Ag₃ complex [Ag{(PDP_H)Ag(PPh₃)₂](OTf) (**2**·OTf), whereas reacts with diethyl phosphite in presence of Li[N(SiMe₃)₂] to yield di-nuclear complex Li₂[(PDP_H)Ag₂{P(O)(OEt)₂}]₂(OTf) (Li₂·**3**·OTf). In **2**, the terminal Ag atoms are three coordinations containing one phosphorous atom from PPh₃ and two nitrogen atoms of PDP_H ligand. The center Ag atom is only two coordinations, binding to the residued pyridyl N atom of PDP_H ligand. In **3**, two silver atoms are bridged by one PDP_H ligand. Treatment of PDP_H with CuCl in presence of NaH afforded heterobimetallic copper–sodium complex [Cu(PDP_H)₂Na(thf)₂] (**4**). The PDP_H ligand in **1-4** are nonplanar, with torsion angles between pyridine and pyrrole rings in the range of 15.8–38.3°. The argentophilic interactions, π...π stacking, and weak interaction of Ag...C(aromatic) are observed in these complexes. Interestingly, treatment of the analogous 2,5-bis(6'-bromo-2'-pyridyl)pyrrole (HPDP_{Br}) with AgOTf affords di-nuclear complex [(HPDP_{Br})Ag]₂(OTf)₂ (**5**·(OTf)₂). Its HPDP_{Br} ligands coordinate to Ag atoms in a head-to-head fashion, and two protonated pyrrole linkages reside on the anti-parallel direction and non-coordinating. Short Ag...Br distances of 3.255–3.390 Å are observed.

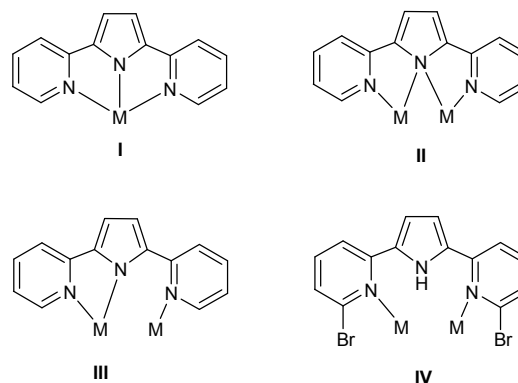
Introduction

Pincer-like ligand belongs to a type of tridentate ligand where the central anionic or neutral donor site is flanked by two neighboring donor groups.^{1,2} It can bind tightly to three adjacent coplanar sites, usually on a transition metal in a meridional configuration. Their metal complexes have attracted interest due to their high stability and ability of catalyzing various organic reactions.³⁻⁵ These include the mono-anionic dipyrilpyrrolide (PDP) ligand based on a pyrrole backbone and two pyridine "arms", shown as in Scheme 1.⁶ PDP ligand combines the π-backbonding capability of 18-π electron N/N/N ligand with the flexible π-properties of pyrrolate donors that behave as versatile π-donor and π-acceptor responses to the metal site π-bonding properties. This ligand has been recognized as an analogue of neutral terpyridine ligand (tpy). In recent years its complexes with late transition metals have received increasing attention. A few opened-shell metals, such as Co(II), Cu(II), Fe(II), Pt(II) and Pd(II), and closed-shell metal of Zn(II) complexes stabilized by dipyrilpyrrolide have been reported.⁶⁻⁸ All of these complexes display coplanar mononuclear geometry (mode I, Scheme 2), where dipyrilpyrrolide act as chelating tridentate ligand binding to metal center in a meridional configuration. It is noted that analogous tpy ligand not only



Scheme 1 structure of dipyrilpyrrolide ligand

Scheme 2 Coordination modes of bispyridylpyrrolides. κ₃-N,N',N'' (I);



μ₂-κ₂(N,N'), κ₂(N',N'') (II); μ₂-κ₂(N,N'), N'' (III); μ₂-N', N'' (IV)

acts as pincer-like ligand to bind to metal center, but also is capable of aggregating metal ions to form novel multi-nuclear

metal complexes. Numerous examples of silver(I) and copper(I) complexes with tpy have been well documented.⁹⁻¹⁵ However, the chemistry of closed-shell d^{10} coinage metal complex containing bispyridylpyrrolide ligand is still unknown. It inspires us to take more interest in studies aimed at the investigation of silver(I) and copper(I) complexes with PDP ligand and their structural variation.

In this paper we report the syntheses and characterizations of a family of silver(I) and copper(I) complexes stabilized by 2,5-bis(2-pyridyl)pyrrolate (HPDP_H) or 2,5-bis(6-bromo-2-pyridyl)pyrrolate (HPDP_{Br}) ligands. Complexes **1-4** feature multi-nuclear metal ions bridged by the twisted PDP_H ligand, and complex **5** displays a novel head-to-head coordination mode of PDP_{Br} ligand. Novel bonding mode of bispyridylpyrrolide in **1-5** are found.

Experimental

General considerations

All manipulations were carried out under nitrogen by standard Schlenk techniques unless otherwise stated. Solvents were purified, distilled and degassed prior to use. ¹H NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400 MHz, and chemical shifts (δ , ppm) were reported with reference to SiMe₄. Infrared spectra (KBr) were recorded on a AVATR360 FT-IR spectrophotometer. The starting 2,5-bis(2'-pyridyl)pyrrolide (HPDP_H)^{16,17} and 2,5-bis(6'-bromo-2'-pyridyl)pyrrolide (HPDP_{Br})^{18,19} were prepared according to literature methods. All of other chemicals were obtained from J&K Scientific Ltd. and used as received.

[PDP_HAg]₃ (**1**)

To a mixture of HPDP_H (33.0 mg, 0.15 mmol) and AgOTf (38.4 mg, 0.15 mmol) in THF (3 mL) was added Et₃N (15.2 mg, 0.15 mmol). The yellow suspension reaction mixture was continued to stir for 2 h and filtered. The filtrate was slowly evaporated to give yellow block crystals which were suitable for X-ray diffraction study. The residue yellow solid of **1** was collected, and washed with water, ethanol and Et₂O. Yield: 25.1 mg (51.2%). ¹H NMR (d^6 -DMSO): δ 8.544 (d, J = 1.2 Hz, 2H), 7.885 (d, J = 3.2 Hz, 2H), 7.802-7.771 (m, 2H), 7.209-7.185 (m, 2H), 6.920 (s, 2H); IR (KBr, cm⁻¹): 3455(w), 3257(m), 1594(s), 1557(m), 1504(m), 1474(s), 1437(s), 1261(vs), 1158(s), 1094(w), 1031(vs), 775(s), 715(w), 636(s), 575(w), 517(m). MS(ESI): m/z 763.25 (M^+ - PDP_H). Anal. Calcd for C₄₂H₃₀Ag₃N₉: C, 51.25; H, 3.07; N, 12.81. Found: C, 51.36; H, 3.35; N, 12.91.

[Ag{(PDP_H)Ag(PPh₃)₂}(OTf)₂](**2**·OTf)

To a mixture of HPDP_H (33.0 mg, 0.15 mmol) and AgOTf (38.4 mg, 0.15 mmol) in THF (3 mL) was added PPh₃ (39.3 mg, 0.15 mmol). The reaction mixture became clear quickly and was continued to stir for 3 h. The filtrate was layered with hexane to give yellow crystals which was suitable for X-ray diffraction study. Yield: 29.5 mg (33.5%). ¹H NMR (d^6 -

DMSO): δ 8.553 (d, J = 2.4 Hz, 4H), 7.888 (d, J = 3.6 Hz, 4H), 7.792 (t, J = 7.6 Hz, 4H), 7.569-7.423 (m, 30H), 7.203 (d, J = 6.0 Hz, 4H), 6.927 (d, J = 0.8 Hz, 4H); ³¹P NMR (d^6 -DMSO): δ 18.30, 14.61 (s, PPh₃). IR (KBr, cm⁻¹): 3446(s), 3257(s), 3048(w), 3003(w), 1590(s), 1557(m), 1516(m), 1476(s), 1460(s), 1437(s), 1260(vs), 1151(s), 1056(s), 1031(vs), 989(m), 948(w), 892(w), 799(m), 774(vs), 714(w), 679(w), 637(s), 617(s), 575(w), 518(m). MS(ESI): m/z 644.52 (M^+ - OTf + H⁺). Anal. Calcd for C₆₅H₅₀Ag₃F₃N₆O₃P₂S: C, 54.30; H, 3.51; N, 5.85. Found: C, 53.21; H, 3.68; N, 5.48.

Li₂[(PDP_H)Ag₂{P(O)(OEt)₂]₂](OTf) (Li₂·3·OTf)

To a mixture of HPDP_H (33.0 mg, 0.15 mmol) and AgOTf (38.4 mg, 0.15 mmol) in THF (3 mL) was added diethyl phosphite (20.7 mg, 0.15 mmol) and LiN(SiMe₃)₂ (0.025 mg, 0.15 mmol). The resulting solution was stirred overnight and filtered. The filtrate was layered with hexane to give yellow crystals which were suitable for X-ray diffraction study. Yield: 21.3 mg (64.5%). ¹H NMR (CDCl₃): δ 8.599 (d, J = 2.4 Hz, 2H), 7.683-7.674 (m, 4H), 7.104 (d, J = 6.4 Hz, 2H), 6.885 (s, 2H), 3.661 (q, J = 10.0 Hz, 8H), 0.993 (t, J = 6.8 Hz, 12H); ³¹P NMR (CDCl₃): δ 115.17, 108.87 (s, -P(O)(OEt)₂). IR (KBr, cm⁻¹): 3444(br, w), 3068(w), 1588(s), 1556(m), 1502(s), 1449(m), 1426(s), 1326(s), 1252(m), 1148(m), 1042(m), 998(w), 946(w), 922(w), 870(w), 778(m), 746(s), 715(w), 691(w). MS(ESI): m/z 790.67 (M - LiOTf + H⁺). Anal. Calcd for C₂₃H₃₀Ag₂N₃O₉P₂SF₃Li₂·5H₂O: C, 28.68; H, 4.19; N, 4.36. Found: C, 27.51; H, 3.83; N, 4.28.

[Cu(PDP_H)₂Na(thf)₂] (**4**)

To a stirred mixture of HPDP_H (132.0 mg, 0.60 mmol) and NaH (14.4 mg, 0.60 mmol) in THF (10 mL) was added CuCl (59.4 mg, 0.6 mmol). Color of solution changed from yellow to orange immediately. After stirring for 4 h, the suspension solution was filtered. The filtrate was layered by hexane to give darkish red crystals which were suitable for X-ray diffraction study. Yield: 30.5 mg (15% based on PDP ligand). ¹H NMR (CDCl₃): δ 8.527 (s, 2H), 7.650-7.627 (m, 2H), 7.582 (d, J = 3.6 Hz, 2H), 7.073 (s, 2H), 6.773 (s, 2H), 3.75 (m, 8H), 1.92 (m, 8H); IR (KBr, cm⁻¹): 3435(br, w), 3079(w), 2846(w), 1598(vs), 1556(m), 1509(s), 1455(m), 1432(s), 1335(s), 1260(w), 1154(m), 1057(m), 1012(w), 959(w), 924(w), 790(w), 755(s), 717(w), 644(w). MS(ESI): m/z 528.00 (M - 2thf + H⁺). Anal. Calcd for C₃₆H₃₆CuN₆NaO₂: C, 64.42; H, 5.41; N, 12.52. Found: C, 64.25; H, 5.38; N, 12.37.

[(HPDP_{Br})Ag]₂(OTf)₂ (**5**·(OTf)₂)

A reaction mixture of HPDP_{Br} (38.0 mg, 0.1 mmol) and AgOTf (25.6 mg, 0.1 mmol) in THF (3 mL) was stirred for 12 h. The yellow suspension solution was formed and filtered. The filtrate was slowly evaporated to give yellow block crystals which were suitable for X-ray diffraction study. The residue yellow solid of **5**·(OTf)₂ was collected and washed with Et₂O. Yield: 34.2 mg (53.5%). ¹H NMR (CDCl₃): δ 11.364 (s, 2H), 7.956 (d, J = 3.2 Hz, 4H), 7.752 (t, J = 6.4 Hz,

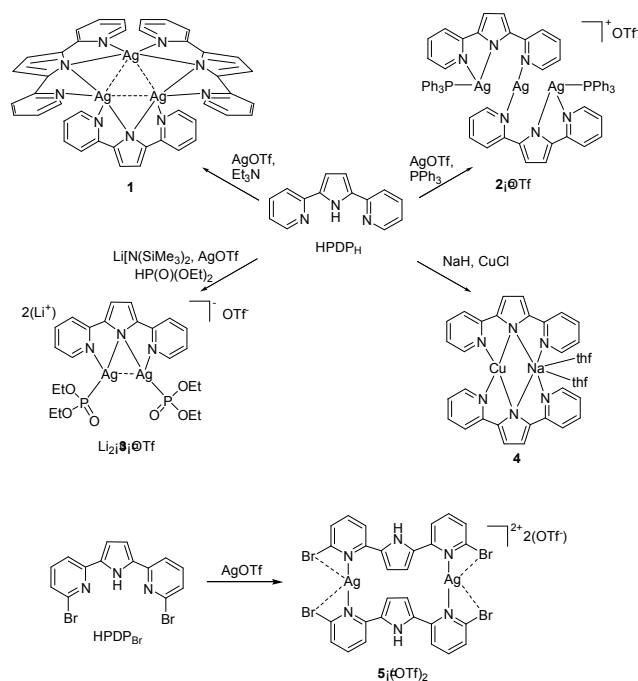
4H), 7.438 (d, $J = 3.2$ Hz, 4H), 6.964 (d, $J = 0.4$ Hz, 4H). IR (KBr, cm^{-1}): 3440(br, w), 3340(w), 3241(w), 3107(w), 1587(s), 1541(s), 1432(vs), 1389(w), 1252(vs), 1163(vs), 1129(m), 1109(m), 1081(m), 1056(w), 998(m), 787(s), 754(m), 633(s), 573(m), 516(m). MS(ESI): m/z 487.08 ($M^{2+} - 2\text{OTf}$). Anal. Calcd for $\text{C}_{15}\text{H}_9\text{AgBr}_2\text{F}_3\text{N}_3\text{O}_3\text{S} \cdot 2\text{H}_2\text{O}$: C, 26.81; H, 1.95; N, 6.25. Found: C, 26.51; H, 1.92; N, 6.10.

X-Ray Crystallography

Diffraction data of **1**, **2**·OTf, $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$, **4**·2(thf), **5**·(OTf)₂ were recorded on a Bruker CCD diffractometer with monochromatized MoK radiation ($\lambda = 0.71073\text{\AA}$). Data collection and reduction were carried out using SAINT and CrysAlisPro program. SADABS was used for the absorption correction.²⁰ Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.²¹ Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were introduced at their geometric positions and refined as riding atoms. In anionic **3**, C21, C22 atoms on diethyl phosphite are disorder with 65/35 occupancy. The co-crystallized THF solvent is found to be disordered, and have been refined with occupancy of 53/47.

Results and Discussion

Synthesis and characterization Treatment of AgOTf with one equivalent of HPDP_H in presence of base, such as Et₃N,



Scheme 3 Syntheses of complexes **1**, **2**·OTf, $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$, **4** and **5**·(OTf)₂

affords yellow precipitate in medium yield (Scheme 3). This reaction is complete within less than 1 h at room temperature.

The isolated solid is identified as tri-nuclear [(PDP_H)Ag]₃ (**1**) by NMR spectrum. **1** is insoluble in common organic solvent, but soluble in the polar solvent such as DMF and DMSO. Upon reaction of mixture of AgOTf and HPDP_H with phosphine, the silver phosphine complexes are formed. As illustrated in Scheme 3, the suspension mixture of AgOTf and HPDP_H reacts with one equivalent of PPh₃ to produce yellow tri-nuclear [Ag{(PDP_H)Ag(PPh₃)₂}(OTf)] (**2**·OTf), whereas reacts with one equivalent of diethyl phosphite in presence of LiN(SiMe₃)₂ to afford yellow di-nuclear Li₂[(PDP_H)Ag₂{P(O)(OEt)₂}]₂(OTf) ($\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$). Complexes of **2**·OTf and $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$ are soluble in THF, CH₂Cl₂, while insoluble in Et₂O and hexane. Attempts to produce other phosphine complexes by treatment of the mixture of AgOTf and HPDP_H with 1,2-bis(diphenylphosphino), 1,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide are failed. Treatment of CuCl with HPDP_H in presence of Et₃N gives a red intractable oily product. NaH instead of Et₃N used to deprotonate HPDP_H, copper-sodium heterobimetallic complex [Cu(PDP_H)₂Na(thf)₂] (**4**) is isolated. Di-nuclear [(HPDP_{Br})Ag]₂(OTf)₂ (**5**·(OTf)₂) is synthesized by treatment of AgOTf with one equivalent of HPDP_{Br} in THF.

Complexes **1**, **2**·OTf, $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$, **4** and **5**·(OTf)₂ are characterized by IR, NMR spectra and X-ray diffraction study. The IR spectra are recorded in the region 4000–450 cm^{-1} on KBr disks. The PDP_H ligand has several distinctive signals, including the weak aromatic C–H stretching at 2976–3107 cm^{-1} . A region from 1420 to 1590 cm^{-1} consists of three or four quite intense signals, corresponding to the in-plane vibrations of the C=C bonds. All above are presented in these five complexes. In addition, **2**·OTf, $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$, and **5**·(OTf)₂ show a strong stretching band at 1253–1278 cm^{-1} due to the triflate group. The ¹H NMR spectrum of **1** in d⁶-DMSO clearly reveals the formation of Ag–N(pyrrolylate) bond, which is indicated by the absence of the imino N–H resonance. Of the four chemical shifts ($\delta = 8.55, 7.88, 7.78$ and 7.20 ppm) for the pyridyl ring hydrogens, the most downfield resonance ($\delta = 8.55$ ppm) is routinely assigned to the H ortho to the nitrogen. The proton resonances of pyrrole ring appear at 6.92 ppm as a doublet. The ¹H NMR spectrum of pyridine and pyrrole protons in **2**·OTf, $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$ and **4** in CDCl₃ closely resemble those in **1**. The ³¹P{¹H} NMR spectra of **2**·OTf and $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$ display multiple peaks 18.3, 14.6 ppm and 115.2, 108.9 ppm attributable to PPh₃ and P(O)(OEt)₂ ligands, respectively. In ¹H NMR spectrum of **5**·(OTf)₂, a resonance of 11.36 ppm is observed, tentatively assigned to the imino proton on the pyrrole ring, which is consistent with the solid state structure.

Description of structure A summary of crystallographic data and experimental details for these five complexes are selected in Table 1. Complex **1** is non-centrosymmetric and crystallizes in the monoclinic space group Cc. As shown in Fig. 1, nearly equilateral triangle Ag₃ core (Ag2–Ag1–Ag3 59.73(3)°, Ag1–Ag2–Ag3 59.04(3)°, Ag1–Ag3–Ag2 61.23(3)°) is supported by three PDP_H ligands in μ_2 -(κ_2 -N,N'),(κ_2 -N,N')

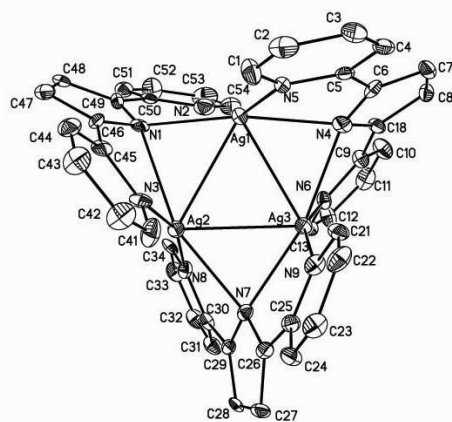


Fig. 1 ORTEP diagram of trinuclear Ag(I) complex **1** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ag1-Ag2 2.9370(12), Ag1-Ag3 2.8732(13), Ag2-Ag3 2.8937(13), Ag1-N1 2.281(9), Ag1-N2 2.659(9), Ag1-N4 2.333(11), Ag1-N5 2.468(10), Ag2-N1 2.494(9), Ag2-N3 2.310(9), Ag2-N7 2.455(10), Ag2-N8 2.283(10), Ag3-N4 2.464(11), Ag3-N6 2.361(9), Ag3-N7 2.369(11), Ag3-N9 2.368(9); Selected bond angles (°): Ag2-Ag1-Ag3 59.73(3), Ag1-Ag2-Ag3 59.04(3), Ag1-Ag3-Ag2 61.23(3), Ag1-N1-Ag2 75.8(2), Ag1-N4-Ag3 73.5(3), Ag2-N7-Ag3 73.7(3), N1-Ag1-N4 169.4(4), N1-Ag1-N5 115.3(3), N4-Ag1-N5 71.2(3), N8-Ag2-N3 163.8(4), N8-Ag2-N7 71.9(3), N3-Ag2-N1 71.3(3), N7-Ag2-N1 159.4(3), N6-Ag3-N9 161.3(3), N6-Ag3-N4 70.6(3), N9-Ag3-N7 71.4(3), N7-Ag3-N4 166.2(3).

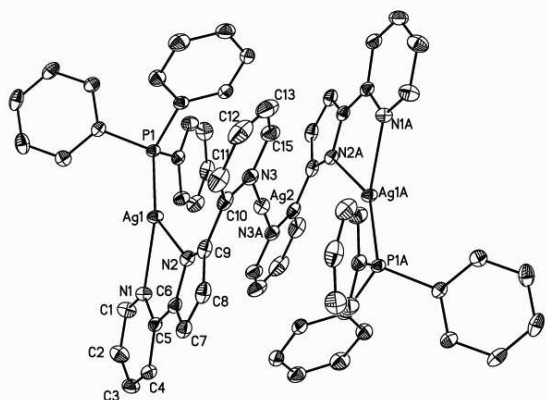


Fig. 2 ORTEP diagram of trinuclear Ag(I) cationic **2** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ag1-N1 2.3645(16), Ag1-N2 2.2163(15), Ag1-P1 2.3503(5), Ag2-N3 2.1275(16), Ag1-Ag2 3.12827(14); Selected bond angles (°): N1-Ag1-P1 132.85(4), N2-Ag1-P1 148.77(4), N1-Ag1-N2 74.28(6), N3-Ag2-N3A 180.00(6), Ag1-Ag2-Ag1A 180.000(3). Symmetry transformations used to generate equivalent atoms: A -x+1, -y+1, -z

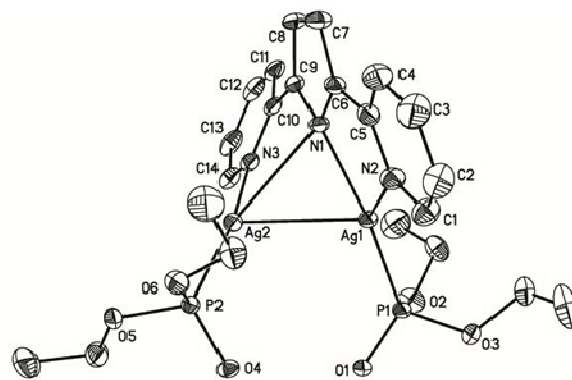


Fig. 3 ORTEP diagram of dinuclear Ag(I) anionic **3** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ag1-N1 2.402(7), Ag1-N2 2.226(8), Ag1-P1 2.325(2), Ag2-N1 2.471(7), Ag2-N3 2.235(8), Ag2-P2 2.316(3), Ag1-Ag2 2.8181(9); Selected bond angles (°): N2-Ag1-P1 146.18(19), N2-Ag1-N1 74.1(3), P1-Ag1-N1 139.28(18), N3-Ag2-P2 149.0(2), N3-Ag2-N1 74.3(3), P2-Ag2-N1 135.78(18).

(II) bonding mode (Scheme 2). This core structure is quite similar to those of Ag₃ N-heterocyclic carbene complexes, [Ag₃(CH₃im(CH₂py))₃(NCCH₃)₂]³⁻, [Ag₃(im(CH₂py)₂)₃]³⁻ and [Ag₃(im(CH₂Mepy)₂)₃]³⁻,^{22,23} and Cu₃ monopyriddyldipyrrole complex.^{24,25} Short Ag-Ag distances in **1** (Ag1-Ag2 2.9370(12) Å, Ag1-Ag3 2.8732(13) Å, Ag2-Ag3 2.8937(13) Å) due to the silver-silver interaction are slightly longer than av. 2.784 Å observed in Ag₃ N-heterocyclic carbene complexes.²² The Ag-N distances in **1** range from 2.281(9) to 2.659(3) Å. To be noticeable, the Ag1-N2(pyridine) bond (2.659(3) Å) is significantly longer than other Ag-N bonds in **1**, indicating there may have no or only a weak interaction between Ag1 and N2. That is consistent with non-centrosymmetric structure of complex **1**. Thus, Ag1 atom is three coordinations, while Ag2 and Ag3 atoms are four coordinations in distorted tetrahedron geometry.

Complex **2**-OTf crystallizes in the monoclinic space group C2/c. Structure of **2** is shown in Fig. 2. A trisilver helicate is present with Ag...Ag distance of 3.12827(14) Å; The μ₂-(κ²-N,N'),N'' (III) bonding mode of PDP_H ligand occurs. The terminal Ag1 and Ag1A atoms are three coordinations and bond to two nitrogen donors of ligand and one triphenylphosphine; the coordination geometry is Y-shape with larger N1-Ag1-P1 (132.85(4) °), N2-Ag1-P1 (148.77(4) °) and smaller N1-Ag1-N2 (74.28(6) °) bond angles. The central Ag2 silver atom is only two coordinate with short Ag-N bonds (2.1275(16) Å) to terminal pyridine rings of each of two ligands and two longer Ag...N contacts to the central pyrrole ring (2.89 Å).

Diethyl phosphite instead of PPh₃ is added into mixture of HPDP_H and AgOTf in presence of Li[N(SiMe₃)₂] to produce binuclear Li₂·3-OTf. As shown in Fig. 3, PDP_H ligand adopts mode II to coordinate two silver atoms. Each silver atom is tri-coordinated by two N atoms from PDP_H ligand and one P atom from diethyl phosphite. Here, the Ag-N(pyrrole) distance (av. 2.437 Å) is longer than that of Ag-N(pyridine)

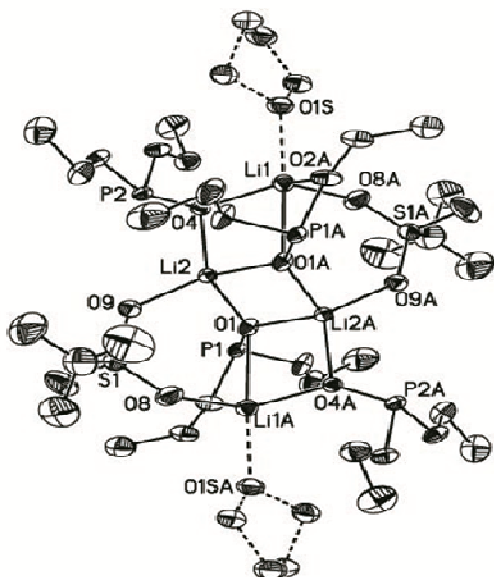


Fig. 4 Coordination geometry of lithium cationic in $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$. Selected bond distances (Å): Li1-O4 1.961(8), Li1-O8A 1.943(8), Li1-O1S 1.935(18), Li1-O1A 2.395(7), Li1-O2A 2.299(8), Li2-O1 1.954(7), Li2-O4 1.933(6), Li2-O9 1.948(6), Li2-O1A 1.939(6).

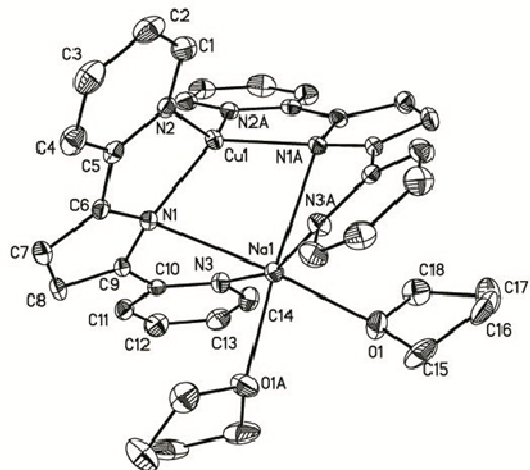


Fig. 5 ORTEP diagram of copper(I) complex **4** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å): Cu(1)-N(1) 2.0581(12), Cu(1)-N(2) 2.0041(12), Na(1)-N(1) 2.6745(13), Na(1)-N(3) 2.4365(12), Na(1)-O(1) 2.3736(13), Cu(1)-Na(1) 2.8927(9). Selected bond angles (°): N1-Cu1-N2 82.61(5), N1-Cu1-N2A, 116.04(5), N1-Cu1-N1A 125.52(7), N2-Cu1-N2A 140.35(7).

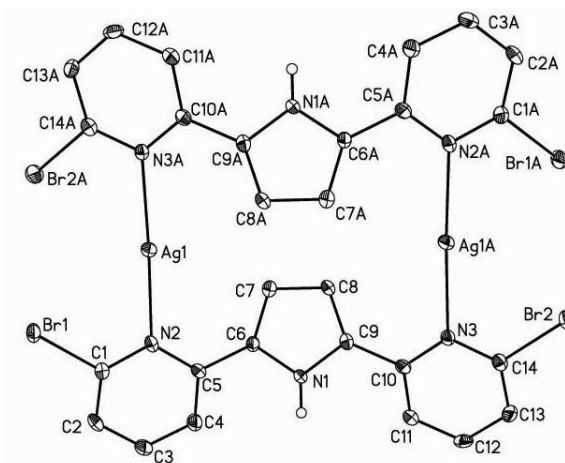


Fig. 6 ORTEP diagram of dinuclear Ag(I) cationic **5** with ellipsoids shown at the 50% probability level. The hydrogen atoms are omitted for clarity except of the pyrrole proton on the nitrogen atom. Selected bond distances (Å): Ag1-N2 2.282(3), Ag1-N3A 2.276(3), Ag3-N23 2.260(3), Ag3-N22B 2.246(3); Selected bond angles (°): N3A-Ag1-N2 177.30(9), N22B-Ag3-N23 173.72(9). Symmetry transformations used to generate equivalent atoms: A $-x+1, -y, -z$; B $-x, -y, -z+1$.

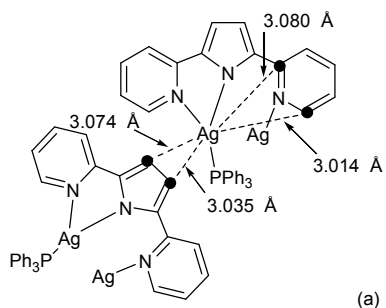
(av. 2.231 Å). The two silver atoms have a distance of 2.8282(9) Å indicating a strong Ag...Ag interaction, which is comparable with Ag-Ag distance found previously. Lithium triflate is cocrystallized in $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$. Its lithium cations are surrounded by oxygen atoms from tetrahydrofuran, diethylphosphite and/or triflate ligand (Fig. 4), resulting in the formation of a tetranuclear ladder-like structure. Li2 and Li2A atoms are four coordinations in tetrahedron geometry with average of Li-O bond distance of 1.943 Å. Li1 and Li1A atoms are coordinated by five oxygen atoms to form a distorted bipyramidal geometry, if longer Li-O bond (Li1-O1A 2.395(7) Å, Li1-O2A 2.299(8) Å) could not be ignored.

In complex **4**, a herical arrangement around the copper(I) and sodium ions is displayed in Fig. 5. Copper(I) atom is chelate-bound by both PDP_H ligands with two nitrogen atoms, while sodium rises to hexa-coordination, additionally bound to two tetrahydrofuran solvent molecules. Within this structural arrangement, the central pyrrole nitrogen atoms N1 and N1A are μ -bridged Cu1 and Na1 with Cu1-N1 and Na1-N1 distances of 2.0581(12) and 2.6745(13) Å, respectively. The Na1-N (pyridine) and Na1-O(thf) bond distances are 2.4365(12) and 2.3736(13) Å, respectively.

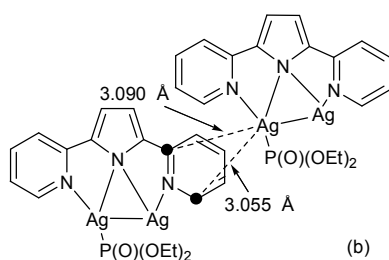
The silver(I) complex supported by bromo-substituted PDP_{Br} ligand is also studied. Complex **5**·(OTf)₂ crystallizes in the triclinic space group P-1 with asymmetric unit containing two one-half of cationic **5** and two OTf anions. X-ray diffraction studies reveal the PDP_{Br} ligands coordinate to Ag atoms only with pyridine nitrogen in a head-to-head fashion (mode IV). Central pyrrole is protonated and non-coordination, residing on the anti-parallel direction. To our knowledge, this is the first report of such coordination mode of bispyridylpyrrolide ligand. The Ag-N bond distances

(2.246(3)-2.282(3) Å) are comparable with those for the Ag-N(pyridine) complexes. The N-Ag-N bond angles are almost linear (N3A-Ag1-N2 177.30(9) and N22B-Ag3-N23 173.72(9)°).

405



(a)



(b)

Scheme 4 (a) Ag...C contact in **2**·OTf; (b) Ag...C contact in $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$; (c) Ag...Br contact in **5**·(OTf)₂

All known bispyridylpyrrolide metal complexes, such as [Co(PDP_H)₂], [M(PDP_H)Cl] (M = Pd, Pt),^{7,8} are mononuclear and rigorously planar, including coplanarity of the three rings of the bispyridylpyrrolides. In comparison, the most noteworthy feature of the structures in this paper is aggregation of coinage metal by nonplanar bispyridylpyrrolides. The two side rings and the pyrrole ring of ligand have twisted to form three interplanar angles with the central ring, which are in the range of 15.8-38.3°, well comparable with those found in the coinage metal terpyridine complexes.¹⁰⁻¹⁵

Potential weak interactions, such as π - π stacking, Ag...C(aromatic) and/or Ag...Br interactions are extensively observed in **1-5**. Weak intermolecular face-to-face π - π stacking is found within the two pendant pyridyls (centroid-centroid distance 3.7957 and 3.8587 Å for **1**, 3.7985, 3.7760 Å for **2**·OTf and 3.901 Å for $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$, 3.734 Å for **5**).

Silver is known to have a remarkable high affinity for some aromatic π -donor system. As shown in Scheme 4, the aromatics in **2**·OTf and $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$ are found η^2 -interacting with the silver ions. The separations varies in the range of 3.01-3.13 Å, and the next closest contacts between Ag and C/N are all over 3.3 Å, which is well comparable with that for polycyclic aromatic silver(I) compounds.²⁶ In the case of **2**·OTf, only terminal Ag is involved in the Ag...C contacts. The contact between Ag and N on the sideways pyridine ring is short (3.080 and 3.014 Å). That could be a cause to make ligand twist and form a large torsion angle of 38.3° between pyrrole and sideways pyridine rings. The intermolecular

contact is perpendicular to the coordination plane of NNP, possibly causing the Ag to be out of this plane by 0.21 Å; The similar intermolecular contact (3.090 Å, 3.055 Å) in $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$ is observed, which is in the opposition direction of Ag...Ag contact. In the case of **5**·(OTf)₂, the strong affinity of the “soft” bromine toward silver atom shows to be very effective in adjusting the coordination framework.²⁷ The distances between silver with the adjacent Br atom within one molecule, such as Ag1...Br3 (3.390 Å), Ag1...Br4 (3.248 Å), Ag2...Br1 (3.253 Å), Ag2...Br2 (3.239 Å), are shorter than their van der Waals radius, which is analogous to that in the silver complex of N-4-bromophenyl-N-4-pyridylurea (3.261 Å).^{27a} PDP_{Br} could hinder aggregation of silver atoms maybe due to the weak steric effect of the ortho-bromine atom. Thus, combination of Ag...Br contacts and steric hinderance of Br in **5** may lead PDP_{Br} in formation of mode **IV**, although the PDP ligand is favor of forming other chelating bonding modes, such as **I**, **II** and **III**.

Conclusion

In summary, we have successfully designed and synthesized silver(I) and copper(I)- bispyridylpyrrolide complexes with different nuclearity. Structural investigation reveals bispyridylpyrrolide ligand has analogous chemistry as terpyridine, being capable of aggregating metal ions to form novel multi-nuclear metal complexes. PDP_H in **1-4** acts as bridging ligand to coordinate two metal atoms in bonding modes **II** and **III**, while PDP_{Br} in **5** binds to silver atoms by face-to-face fashion (bonding mode **IV**). It seems likely that the bonding flexibility of central pyrrole nitrogen and the range of potential molecular interactions, such as π - π stacking, Ag...Br, Ag...C interactions, directly lead the bispyridylpyrrolide ligand to change bonding mode, and to rotate away from planarity to accommodate a bridging structural role.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (project 21001118), China Postdoctoral Science Foundation (2011M500129) and the Postdoctoral Science Foundation of Central South University. This material is available free of charge via the Internet at <http://pubs.acs.org>.

480

Notes and references

Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, P. R. China. Fax: 86 731 88879616; Tel: 86 731 88879616; E-mail: xyyi@csu.edu.cn

† Electronic Supplementary Information (ESI) available. CCDC reference numbers 963075-963079 for complex **1**, **2**·OTf, $\text{Li}_2\cdot\mathbf{3}\cdot\text{OTf}$, **4** and **5**·(OTf)₂, respectively. see DOI: 10.1039/b000000x/.

- 1 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020-1024.
- 2 J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327-352.
- 3 M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759-1792.
- 4 M. G. Scheibel, B. Askevold, F. W. Heinemann, E. J. Reijerse, B. de Bruin and S. Schneider, *Nat. Chem.*, 2012, **4**, 552-558.

- 5 N. Selander and K. J. Szabó, *Chem. Rev.*, 2011, **111**, 2048–2076.
- 6 J. W. Ciszek, Z. K. Keane, L. Cheng, M. P. Stewart, L. H. Yu, D. Natelson and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 3179–3189.
- 500 7 G. H. Imler, Z. Lu, K. A. Kistler, P. J. Carroll, B. B. Wayland and M. J. Zdzilla, *Inorg. Chem.* 2012, **51**, 10122–10128.
- 8 F. Hein and U. Beierlein, *Pharm. Zentralhalle Dtschl.*, 1957, **96**, 401–421.
- 9 M. Al-Anber, B. Walfort, S. Vatsadze and H. Lang, *Inorg. Chem. Comm.*, 2004, **7**, 799–802.
- 505 10 Y. Cui and C. He, *J. Am. Chem. Soc.*, 2003, **125**, 16202–16203.
- 11 G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.*, 1998, 2659–2660.
- 12 E. C. Constable, T. Kulke, M. Neuburger and M. Zehnder, *Chem. Commun.* 1997, 489–490.
- 510 13 Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 2007, **360**, 1414–1423.
- 14 (a) H. Feng, X.-P. Zhou, T. Wu, D. Li, Y.-G. Yin and S. W. Ng, *Inorg. Chim. Acta*, 2006, **359**, 4027–4035. (b) Z. Ma, Y.-P. Xing, M. Yang, M. Hu, B.-Q. Liu, M. F. C. G. da Silva and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2009, **362**, 2921–2926.
- 515 15 M. J. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs and N. W. Alcock, *Chem. Eur. J.*, 2002, **8**, 2225–2238.
- 16 H. Schindlbauer, *Monatsh. Chem.*, 1968, **99**, 1799–1807.
- 520 17 R. A. Jones, M. Karatza, T. N. Voro, P. U. Covicir, A. Franck, O. Ozturk, J. P. Seaman, A. P. Whitmore and D. J. Williamson, *Tetrahedron*, 1996, **52**, 8707–8724.
- 18 D. C. Owsley, J. M. Nelke and J. J. Bloomfield, *J. Org. Chem.*, 1973, **38**, 901–903.
- 525 19 Z. Zhang, J. M. Lim, M. Ishida, V. V. Roznyatovskiy, V. M. Lynch, H.-Y. Gong, X. Yang, D. Kim and J. L. Sessler, *J. Am. Chem. Soc.*, 2012, **134**, 4076–4079.
- 20 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, 1997.
- 21 G. M. Sheldrick, *SHELXTL-Plus V5.1 Software Reference Manual*; Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
- 530 22 (a) V. J. Catalano and S. J. Horner, *Inorg. Chem.*, 2003, **42**, 8430–8438; (b) V. J. Catalano and M. A. Malwitz, *Inorg. Chem.*, 2003, **42**, 5483–5485; (c) V. J. Catalano and A. L. Moore, *Inorg. Chem.*, 2005, **44**, 6558–6566.
- 535 23 (a) P. A. Leach, S. J. Geib and N. J. Cooper, *Organometallics*, 1992, **11**, 4367–4370; (b) J. C. Garrison, C. A. Tessier and W. J. Youngs, *J. Organomet. Chem.*, 2005, **690**, 6008–6020.
- 24 V. J. Catalano, L. B. Munro, C. E. Strasser and A. F. Samin, *Inorg. Chem.*, 2011, **50**, 8465–8476.
- 540 25 J. G. Andino, J. A. Flores, J. A. Karty, J. P. Massa, H. Park, N. P. Tsvetkov, R. J. Wolfe and K. G. Caulton, *Inorg. Chem.*, 2010, **49**, 7626–7628.
- 26 M. Munakata, L.-P. Wu, G.-L. Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and N. Maeno, *J. Am. Chem. Soc.*, 1999, **121**, 4968–4976.
- 545 27 (a) S. K. Chandran, R. Thakuria and A. Nangia, *CrystEngComm*, 2008, **10**, 1891–1898; (b) M. D. Ward, S. M. Couchman and J. C. Jeffery, *Acta Cryst.*, 1998, **C54**, 1820–1823.

Table 1. Crystallographic data and experimental details for **1**, **2**·OTf and **Li₂·3**·OTf, **4** and **5**·(OTf)₂

Complexes	1	2 ·OTf	Li₂·3 ·OTf	4	5 ·(OTf) ₂
Formula	C ₄₂ H ₃₀ Ag ₃ N ₉	C ₆₅ H ₅₀ Ag ₃ F ₃ N ₆ O ₃ P ₂ S	C ₅₄ H ₇₆ Ag ₄ F ₆ Li ₄ N ₆ O ₂₀ P ₄ S ₂	C ₃₆ H ₃₆ CuN ₆ NaO ₂	C ₃₀ H ₁₈ Ag ₂ Br ₁ F ₆ N ₆ O ₆ S ₂
fw	984.36	1437.72	1890.45	671.24	1272
crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
space group	Cc	C2/c	P-1	Fdd2	P-1
a, Å	15.055(3)	19.8842(3)	12.4463(2)	11.6882(3)	7.8073(16)
b, Å	19.328(4)	17.3938(3)	12.9013(2)	30.6434(8)	15.310(3)
c, Å	12.632(2)	17.4070(2)	14.0856(2)	18.0484(5)	16.630(3)
α, deg	90	90	66.1580(10)	90	110.57(3)
β, deg	104.687(2)°	108.2390(10)°	69.5560(10)	90	98.30(3)
γ, deg	90	90	74.9330(10)	90	96.19(3)
V, Å ³	3555.6(11)	5717.94(15)	1919.76(5)	6464.3(3)	1814.4(6)
Z	4	4	1	8	2
ρ _{calc} , g cm ⁻³	1.839	1.670	1.635	1.379	2.328
T, K	296(2)	120(2)	296(2)	120(2)	120(2)
μ, mm ⁻¹	1.683	1.174	1.224	0.732	5.684
no. of refln.	9592	29949	22224	7241	15452
no. of indep. refln.	4730	6557	7469	2976	8113
R _{int}	0.0561	0.0180	0.0163	0.0137	0.0211
GoF	0.975	1.024	1.010	1.049	1.059
R ₁ , wR ₂ [I > 2σ(I)]	0.0506, 0.1118	0.0205, 0.0671	0.0361, 0.1047	0.0178, 0.0530	0.0266, 0.0585
R ₁ , wR ₂ (all data)	0.0644, 0.1212	0.0257, 0.0793	0.0459, 0.1141	0.0180, 0.0532	0.0355, 0.0679

