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COVER ARTICLE Habata *et al.* Argentivorous molecules with two kinds of aromatic side-arms: intramolecular competition between side-arms

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Introduction

Weak interactions such as metal-cation– π^1 and CH– π^2 interactions are important not only in supramolecular chemistry, but also in biochemistry. In some cases, weak interactions are key interactions in supramolecular chemistry.

side-armst

induced UV-vis spectral changes.

Recently, we reported that tetra-armed and double-armed cyclens act as argentivorous molecules by $Ag^+-\pi$ and $CH-\pi$ interactions.³⁻⁵ Ag- π and $CH-\pi$ interactions in solution were shown based on the chemical shift changes in the ¹H NMR spectra of the protons at the 2'- and 6'-positions in the aromatic side-arms. In a continuation of our previous work, we prepared new tetra-armed cyclens with two kinds of aromatic side-arms to answer the following questions. (i) When a tetra-armed cyclen with two kinds of substituted-benzyl groups, *i.e.*, 3',5'-difluorobenzyl and 4'-methylbenzyl groups, which have electron-withdrawing groups and electron-donating groups, respectively, forms an Ag⁺ complex, are the chemical shift changes of the protons at the 2'- and 6'-positions dependent on the electron density on the substituted benzenes? (ii) When

a combination of two kinds of aromatic rings, such as 3',5'difluorobenzyl and 1'-naphthylmethyl groups, and 3',5'-difluorobenzyl and 9'-anthrylmethyl groups, is introduced into a cyclen, do the aromatic rings with higher electron densities preferentially cover the Ag^+ ions incorporated into the ligand cavities? Here, we report the structures in the solid-state and in solution of Ag^+ complexes with argentivorous molecules with two kinds of aromatic side-arms.

Results and discussion

Argentivorous molecules with two kinds of aromatic

side-arms: intramolecular competition between

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Three tetra-armed cyclens with two kinds of side-arms, 3',5'-difluorobenzyl/4'-methylbenzyl, 3',5'-difluorobenzyl/1'-naphthylmethyl, and 3',5'-difluorobenzyl/9'-anthrylmethyl groups, were prepared by reductive amination of 1,7-bis(3',5'-difluorobenzyl)-1,4,7,10-tetraazacyclododecane and the corresponding aromatic aldehydes in the presence of NaBH(OAc)₃. The X-ray structures of the Ag⁺ complexes and Ag⁺ion-induced ¹H NMR spectral changes suggest that (i) the chemical shift changes of the protons at the 2'- and 6'-positions in the 3',5'-difluorobenzyl/4'-methylbenzyl side-arms are dependent on the electron density on the adjacent substituted benzenes, and (ii) in the tetra-armed cyclens with 3',5'-difluoro-

benzyl/1'-naphthylmethyl and 3',5'-difluorobenzyl/9'-anthrylmethyl groups as side-arms, electron-rich

aromatic rings preferentially cover the Ag⁺ ions incorporated into the ligand cavities, and 3',5'-difluoro-

benzyl groups do not participate in the Aq^+ interactions. The log K values were estimated using Aq^+ -ion-

New tetra-armed cyclens (1, 2, and 3 in Fig. 1) were prepared by the reductive amination of 1,7-bis(3,5-difluorobenzyl)-1,4,7,10-tetraazacyclododecane⁵ and the corresponding aromatic aldehydes. The structures of the new armed cyclens were confirmed by ¹H NMR spectroscopy, FAB-MS, elemental analysis, and X-ray crystallography (Fig. S2–S7 in the ESI[†]).



Fig. 1 Argentivorous molecules with two kinds of side-arms.

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 $[\]dagger$ Electronic supplementary information (ESI) available. CCDC CCDC 917307–917313. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00034f

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Fig. 2 Electrostatic potential maps of (a) 1,3-difluoro-4-methylbenzene, (b) 1,4-dimethylbenzene, (c) 1-methylnaphthalene, and (d) 9-methylanthracene.



Fig. 3 X-ray structure of $1/AgCF_3SO_3$ [(a) top and (b) side views]. $CF_3SO_3^-$ is omitted. Meshed hydrogen atoms are the hydrogens at the 2'- and 6'-positions (the H_b and H_c protons, respectively, in Fig. 1).

Fig. 2 shows electrostatic potential maps, calculated using the HF/6-31G(*) method,⁵ of the aromatic rings we used. The electrostatic potential maps show that the electron densities in 1,4-dimethylbenzene (b), 1-methylnaphthalene (c) and 9-methylanthracene (d) are higher than that in 1,3-difluoro-4-methylbenzene (a). In addition, the areas of higher electron density in 1-methylnaphthalene and 9-methylanthracene are wider than those in 1,4-dimethylbenzene. We therefore expected that 4'-dimethylbenzyl, 1'-naphthylmethyl, and 9'-anthrylmethyl side-arms would cover the Ag^+ ions incorporated into the ligand cavities, but a 3',5'-difluorobenzyl sidearm would not.

Fig. 3 shows the X-ray structure of the $1/\text{AgCF}_3\text{SO}_3$ complex. Contrary to our expectations, the four aromatic side-arms cover the Ag⁺ ion incorporated into the ligand cavity. The Ag1–C22 (C37) and Ag1–C15(C30) distances are 3.295(3.215) and 3.400 (3.537) Å, respectively. The distances indicate that the strength of the Ag⁺– π interaction depends on the electron densities on the aromatic rings. In addition, the distances between the hydrogen atoms at the 2'- and 6'-positions of the side-arms and the adjacent benzene planes are in the range 2.687–2.905 Å. The distances are typical CH– π bond distances.^{2d,4} In contrast, the side-arms in the 1/Cu(CF₃SO₃)₂ complex never cover the Cu²⁺ ions incorporated into the ligand cavities (Fig. S8 in the ESI†).

Fig. 4 shows the X-ray structure of the $2/\text{AgBF}_4$ complex. When 1'-naphthyl groups are used as side-arms with 3',5'difluorobenzyl groups, only 1'-naphthylmethyl groups cover the Ag⁺ ions. The C25–Ag1 and C36–Ag1 distances are 2.432 and 3.325 Å, respectively. In addition, the H36–naphthalene (including the C25 carbon)-plane distance is 2.797 Å. The X-ray data suggest that the naphthalene side-arms cover the Ag⁺ ions by Ag⁺– π interactions, and there are intramolecular CH– π interactions between the naphthalene side-arms. The X-ray data



Fig. 4 X-ray structure of $2/AgBF_4$ [(a) top and (b) side views]. $CF_3SO_3^-$ is omitted. Meshed hydrogen atoms are the protons at the 2'- and 6'-positions of 3',5'-difluorobenzyl side-arms (H_h protons in Fig. 1).



Fig. 5 X-ray structure of $3/AgCF_3SO_3$ [(a) top and (b) side views]. $CF_3SO_3^-$ is omitted. Meshed hydrogen atoms are the protons at the 2'- and 6'-positions of 3',5'-difluorobenzyl side-arms (H_f protons in Fig. 1).

support our expectation of intramolecular competition between aromatic side-arms.

The X-ray structure of the 3/AgCF₃SO₃ complex is shown in Fig. 5. In this complex, two anthracene side-arms cover the Ag^+ ions incorporated into the ligand cavities. The C51-Ag1 and C29–Ag1 distances are 2.591 and 3.102 Å, respectively, and the dihedral angle between the anthracene planes is 32.85°. The dihedral angle is comparable with that in a double-armed cyclen with two anthrylmethyl groups.5 The two 3',5'-difluorobenzyl side-arms do not participate in Ag⁺- π interactions. The X-ray data also support the expectation of intramolecular competition between aromatic side-arms. The distances between the Ag ions and the mean planes of the four nitrogen atoms in 1, 2, and 3 are 1.173, 1.198, and 1.240 Å, respectively. The distances are shorter than that of the cyclen having 2-(methylsulfanyl)ethyl groups as side-arms (1.346–1.329 Å) which have strong binding ability towards Ag⁺ ions.⁶ The results indicate that the aromatic side-arms with higher electron density are more strongly bound to Ag⁺ ions.



Fig. 6 Ag⁺-ion-induced ¹H NMR spectral changes of 1 (in CD₂Cl₂/CD₃OD).



To confirm the structures of the Ag^+ complexes in solution, Ag⁺-ion-induced ¹H NMR chemical shift changes were investigated. As shown in Fig. 6, the protons at the 2'- and 6'-positions of the 3',5'-difluorobenzyl and 4'-methylbenzyl side-arms shifted to higher field by ca. 0.25 and 0.82 ppm, respectively. These chemical shift changes indicate that the protons at the 2'- and 6'-positions are located in the shielding area of the adjacent aromatic rings, *i.e.*, the protons at the 2'- and 6'-positions of the 3',5'-difluorobenzyl groups are significantly shifted by the adjacent 4'-methylbenzyl groups, which have higher electron densities, and the protons at the 2'- and 6'-positions of the 4'-methylbenzyl groups are not shifted so much by the adjacent 3',5'-difluorobenzyl groups, which have lower electron densities.

A ROESY spectrum was obtained (Fig. 7) to confirm the conformations of the side-arms in solution. A cross-peak was observed between the H_d protons of the 3',5'-difluorobenzyl groups and the H_a protons of the 4'-methylbenzyl groups in the side-arms. This result clearly indicates that the



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Fig. 8 Ag⁺-ion-induced UV-vis spectral changes of 1. [1] = 1.0×10^{-4} mol L⁻¹ (CH₂CN).

conformations of the aromatic side-arms in solution are similar to those in the X-ray structure. Ag⁺-ion-induced ¹H NMR chemical shift changes of 2 and 3 were also examined. Titration experiments using 2 indicate that the H_g protons of the 1'-naphthylmethyl side-arms and the H_h protons of the 3',5'-difluorobenzyl side-arms shifted to higher field by ca. 0.31 and 0.91 ppm, respectively (Fig. S10⁺). When 3 was used as the ligand for titration experiments, the H_f proton of the 3',5'difluorobenzyl side-arms shifted to higher field by ca. 0.95 ppm (Fig. S11⁺). The X-ray structures of the 2/AgBF₄ and 3/AgCF₃SO₃ complexes indicate that the meshed hydrogen atoms in Fig. 4 and 5 are located in the shielding area of the nearest neighbor aromatic rings. The X-ray structures and ¹H NMR titration experiments strongly support the suggestion that the structures of the complexes in solution are similar to the solid-state structures.

Fig. 8 and Fig. S12–S13 in the ESI⁺ show Ag⁺-ion-induced UV spectral changes of 1 (and 2 and 3). Nonlinear leastsquares analyses of the titration profiles (absorbance versus equivalents of Ag⁺ added, see Fig. S14–S16 in the ESI⁺) clearly indicated the formation of 1:1 complexes, and allowed us to estimate the association constants. The log K values between the ligands (1, 2, and 3) and Ag^+ ions in CH_3CN were estimated to be ca. 6.6, 8.4, and 10.1, respectively.

To visualize the Ag^+ - π interactions, the isosurfaces of the LUMOs and HOMOs of the Ag⁺ complexes were calculated using the B3LYP/3-21G(*) theoretical level.⁷ Fig. 9 and Fig. S17 in the ESI⁺ show the LUMO (mesh) and HOMOs (solid) of the X-ray structures of the $1/Ag^+$ - $3/Ag^+$ complexes. In all cases, the LUMO of the Ag⁺ ion is distorted by interaction with the HOMOs of the aromatic side-arms. These graphics clearly support $Ag^+ - \pi$ interactions between the Ag^+ ion and the aromatic side-arms.

Conclusions

In conclusion, we demonstrated that tetra-armed cyclens with two kinds of aromatic side-arms behave like argentivorous



Fig. 9 LUMO (mesh), HOMO[-4], HOMO[-5], HOMO[-6], and HOMO[-7] (solid) from X-ray structures of Ag⁺ complexes with 1 (the isosurface value is 0.032 au).

molecules in the solid-state and in solution; aromatic sidearms with high electron densities preferentially cover the Ag⁺ ions incorporated into the ligand cavities, whereas aromatic side-arms with lower electron densities do not. This is the first example showing the relative strengths of the Ag⁺– π interactions between different aromatic rings within a molecule.

Experimental

Melting points were obtained with a Mel-Temp capillary apparatus and not corrected. FAB-MS was performed using a JEOL 600 H spectrometer. ¹H NMR spectra were measured in $CDCl_3$ on a JEOL ECP400 (400 MHz) spectrometer. Cold ESI-MS were recorded on a JEOL JMS-T100CS spectrometer.

General procedures for the reaction of 1,7-bis(3',5'difluorobenzyl)-1,4,7,10-tetraazacyclododecane with aromatic aldehydes

After stirring a mixture of 1,7-bis(3',5'-difluorobenzyl)-1,4,7,10tetraazacyclododecane (1.0 mmol) and aromatic aldehydes (4.1 mmol) in dry 1,2-dichloroethane (12 mL) at room temperature for 1 day under an argon atmosphere (1 MP), NaBH(OAc)₃ (4.0 mmol) was added and the mixture was stirred for 1 day at room temperature. Saturated aqueous NaHCO₃ was added and the aqueous layer was extracted with chloroform thrice. The combined organic layer was washed with water, dried over Na₂SO₄, and concentrated. The residual solid was purified by column chromatography on silica-gel. The main fraction was recrystallized from acetonitrile to give the following products.

1,7-Bis(3',5'-difluorobenzyl)-4,10-bis(4"-methylbenzyl)-1,4,7,10**tetraazacyclododecane** (1). An eluent for column chromatography: toluene–ethanol–ammonia = 5:2:0.07. Yield 54%. Mp: 111.7–112.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 4H), 6.91(d, *J* = 6.4 Hz, 4H), 6.66 (tt, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 2H), 3.39 (s, 4H), 3.34 (s, 4H), 2.64 (s, 8H), 2.63 (s, 8H), 2.30 (s, 6H). FAB-MS (*m*/*z*) (matrix: DTT-TG = 1:2): 633 ([M + 1]⁺, 100%). Anal. Calcd for C₃₈H₄₄N₄F₄: C, 72.13; H, 7.01; N, 8.85. Found: C, 72.19; H, 7.05; N, 8.79. **1,7-Bis(3',5'-difluorobenzyl)-4,10-bis(1"-naphthylmethyl)-1,4,7,10-tetraazacyclododecane (2).** An eluent for column chromatography: toluene. Yield 27%. Mp: 95.1–96 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.37–8.30 (m, 2H), 7.86–7.80 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.50–7.44 (m, 4H), 7.37 (dd, *J*₁ = 8.0 Hz, *J*₂ = 7.2 Hz, 2H), 6.76 (d, *J* = 6.4 Hz, 4H), 6.61 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 2H), 3.88 (s, 4H), 3.28 (s, 4H), 2.74 (t, *J* = 4.8 Hz, 8H), 2.66 (t, *J* = 4.8 Hz, 8H). FAB-MS (*m*/*z*) (matrix: DTT–TG = 1:2): 705 ([M + 1]⁺, 75%). Anal. Calcd for C₄₄H₄₄N₄F₄: C, 74.98; H, 6.29; N, 7.95. Found: C, 75.19; H, 6.41; N, 7.99.

1,7-Bis(9'-anthrylmethyl)-4,10-bis(3",5"-difluorobenzyl)-1,4,7,10-tetraazacyclododecane (3). An eluent for column chromatography: chloroform-methanol = 20:1. Yield 10%. Mp: 173.8–174.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.55 (d, *J* = 8.0 Hz, 4H), 8.38 (s, 2H), 7.98 (d, *J* = 8.0 Hz, 4H), 7.54–7.41 (m, 8H), 6.58 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 2H), 6.52 (d, *J* = 6.4 Hz, 4H), 4.38 (s, 4H), 3.06 (s, 4H), 2.77 (t, *J* = 5.6 Hz, 8H), 2.56 (t, *J* = 5.6 Hz, 8H). FAB-MS (*m*/*z*) (matrix: DTT-TG = 1:2): 805 ([M + 1]⁺, 60%). Anal. Calcd for C₃₈H₄₄N₄F₄0.5H₂O: C, 76.73; H, 6.07; N, 6.88. Found: C, 76.77; H, 6.09; N, 7.01.

General procedure of the preparation of metal complexes

 $1/\text{AgCF}_3\text{SO}_3$ complex. 1 (0.0151 mmol) in chloroform (1 mL) was added to the corresponding metal salt (AgCF}_3SO_3, AgBF_4, or Cu(CF}_3SO_3)_2) (0.0153 mmol) in methanol (1 mL). Crystals were obtained quantitatively on evaporation of the solvent. Mp: 191–193 °C (dec.). Anal. Calcd for C_{39}H_{44}N_4O_3SF_7Ag: C, 52.65; H, 4.98; N, 6.30. Found: C, 52.98; H, 5.05; N, 6.01.

 $1/Cu(CF_3SO_3)_2$ complex. Mp: 308–309.5 °C (dec.). Anal. Calcd for $C_{40}H_{44}N_4O_6S_2F_{10}Cu$: C, 48.31; H, 4.46; N, 5.63. Found: C, 48.29; H, 4.57; N, 5.89.

 $2/\text{AgBF}_4$ complex. Mp: 196–198 °C (dec.). Anal. Calcd for $C_{49}H_{44}N_4BF_8Ag$ ·0.5CH₃CN: C, 58.75; H, 4.98; N, 6.85. Found: C, 58.76; H, 5.09; N, 6.93.

 $3/\text{AgCF}_3SO_3$ complex. Mp: 218–219 °C (dec.). Anal. Calcd for $C_{53}H_{48}N_4O_3SF_7Ag$: C, 59.95; H, 4.56; N, 5.28. Found: C, 59.86; H, 4.63; N, 4.93.

X-ray structure determination

Crystals of the AgCF₃SO₃, AgBF₄, and Cu(CF₃SO₃)₂ complexes with ligands were mounted on top of a glass fiber, and data collections were performed using a Bruker SMART CCD area diffractometer at 90–298 K. Data were corrected for Lorentz and polarization effects, and absorption corrections were applied using the SADABS⁸ program. Structures were solved by a direct method and subsequent difference-Fourier syntheses using the program SHELEX.⁹ All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions and then refined using $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. The crystallographic refinement parameters of the complexes are summarized in Table 1.

| Table 1 | Crystal data of | 1, 1/AgCF ₃ SO ₃ , | 1/Cu(CF ₃ SO ₃) ₂ , 2, 2/AgBI | F_4 , 3 , and 3 /Ag CF ₃ SO ₃ |
|---------|-----------------|--|---|---|
|---------|-----------------|--|---|---|

| Compound | 1 | 1/AgCF ₃ SO ₃ | $1/Cu(CF_3SO_3)_2$ | 2 | $2/\mathrm{AgBF}_4$ | 3 | 3/AgCF ₃ SO ₃ |
|---|---|--|---|--------------------------------|--|------------------------------------|---|
| Formula <i>M</i> r | C ₃₈ H ₄₄ F ₄ N ₄ 632.77 | $\begin{array}{c} C_{78}H_{89}Ag_2F_{14}N_8O_7S_2\\ 1796.43 \end{array}$ | C ₄₄ H ₅₁ CuF ₁₀ N ₆ O ₇ S ₂ 1093.57 | $C_{44}H_{44}F_4N_4$ 704.83 | C ₄₆ H ₄₇ AgBF ₈ N ₅ 940.57 | $C_{52}H_{48}F_4N_4$ 804.94 | C ₅₃ H ₄₈ AgF ₇ N ₄ O ₃ S 1061.88 |
| Temperature | 90 K | 298 K | 90 K | 298 K | 223 K | 90 K | 223 K |
| Wavelength | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic | Triclinic | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | P1 | P2(1)/c | P1 | P1 | P2(1)/c | P1 | P2(1)/c |
| a(Å) | 9.7254(8) | 10.0071(5) | 11.7735(17) | 9.1992(10) | 10.0718(9) | 8.8124(8) | 14.8401(8) |
| b(A) | 11.1668(10) | 15.1936(7) | 13.944(2) | 10.3017(11) | 30.925(3) | 9.6778(9) | 14.3569(8) |
| c(Å) | 15.5750(14) | 27.0539(13) | 16.541(2) | 10.9195(11) | 16.7058(11) | 13.3655(12) | 23.2128(11) |
| $\alpha(\circ)$ | 91.609(2) | 90 | 108.029(3) | 79.597(2) | 90 | 86.321(2) | 90 |
| $\beta(\circ)$ | 99.574(2) | 93.5910(10) | 106.344(3) | 88.318(2) | 126.958(4) | 71.759(2) | 112.169(3) |
| $\gamma(\circ)$ | 93.894(2) | 90 | 102.841(3) | 67.609(2) | 90 | 63.608(2) | 90 |
| $V(Å^3)$ | 1662.7(3) | 4105.3(3) | 2331.1(6) | 940.18(17) | 4157.9(6) | 965.98(15) | 4580.1 |
| Z | 2 | 2 | 2 | 1 | 4 | 1 | 4 |
| D calculated (Mg m ⁻³) | 1.264 | 1.453 | 1.558 | 1.245 | 1.503 | 1.384 | 1.540 |
| μ/mm^{-1} | 0.090 | 0.616 | 0.656 | 0.087 | 0.561 | 0.094 | 0.565 |
| F(000) | 672 | 1842 | 1128 | 372 | 1982 | 424 | 2176 |
| Crystal size | 0.31 	imes 0.20 	imes | 0.29 	imes 0.24 	imes 0.15 | 0.29 	imes 0.24 	imes 0.15 | 0.52 	imes 0.38 	imes | $0.72 \times 0.45 \times$ | 0.42 	imes 0.18 	imes | $0.77 \times 0.75 \times 0.39$ |
| (mm^3) | 0.19 | | | 0.29 | 0.39 | 0.18 | |
| $\hat{\theta}$ range for data collection | 1.83 to 28.30 | 1.51 to 28.35 | 1.40 to 28.36 | 1.90 to 28.35 | 1.32 to 28.34 | 1.61 to 28.32 | 1.48 to 28.33 |
| Index ranges | -9 < h < 12 | -13 < <i>h</i> < 13 | $-15 \le h \le 15$ | -9 < h < 12 | $-12 \le h \le 13$ | -6 < h < 11 | $-19 \le h \le 13$ |
| 8 | $-14 \le k \le 13$ | $-20 \le k \le 12$ | -9 < k < 18 | -12 < k < 13 | $-41 \le k \le 40$ | -12 < k < 12 | $-19 \le k \le 17$ |
| | $-20 \le l \le 20$ | -36 < l < 35 | -22 < l < 22 | $-13 \le l \le 14$ | -22 < l < 22 | -17 < l < 17 | $-30 \le l \le 30$ |
| Reflections | 11 994 | 30 203 | 16 839 | 7050 | 31 007 | 7261 | 33 769 |
| Independent | 8151 | 10 249 | 11 301 | 4629 | 10 345 | 4723 | 11 379 |
| reflections | [R(int) = 0.0252] | [R(int) = 0.0745] | [R(int) = 0.0397] | [R(int) = 0.0126] | [R(int) = 0.0264] | [R(int) = 0.0221] | [R(int) = 0.0202] |
| Max. and min. | 0.9833. | 0.9155. 0.8426 | 0.9104. 0.8336 | 0.9752. | 0.8129. 0.6867 | 0.9834. | 0.8094. 0.6715 |
| transmission | 0.9722 | , | | 0. 0.9562 | , | 0.9612 | |
| Refinement method | Full-matrix least-squares | Full-matrix least-squares on F^2 | Full-matrix least- squares on <i>F</i> ² | Full-matrix least-squares | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least- squares on <i>F</i> ² |
| Data/mostmints/ | 011 F | 10.040/0/507 | 11 201/0/025 | 011 F 4C00/0/025 | 10 245/26/551 | 011 F 4702/0/071 | 11 270/0/670 |
| Data/Testfamts/ | 8151/0/41/ | 10 249/0/307 | 11 391/0/635 | 4629/0/235 | 10 343/30/331 | 4/23/0/2/1 | 11 3/9/0/0/0 |
| Candman of fit | 1 000 | 0.020 | 0.720 | 1 024 | 1 050 | 0.002 | 1 054 |
| Goodness-oi-iit | 1.029 | 0.828 | 0.739 | 1.034 | 1.050 | 0.983 | 1.054 |
| OII F | 0.0510 | 0.0516.0.0000 | 0.0011 0.1002 | 0.0565 | 0.0261.0.0041 | 0.0550 | 0.0000 0.0700 |
| Final <i>R</i> indices $[I > 2\sigma(I)] R_1,$ wP | 0.0518, 0.1208 | 0.0516, 0.0882 | 0.0641, 0.1603 | 0.0565, 0.1475 | 0.0361, 0.0941 | 0.0552, 0.1314 | 0.0298, 0.0796 |
| R indices (all data) R w R | 0.0801, | 0.1097, 0.1009 | 0.1011, 0.1821 | 0.0954, | 0.0448, 0.0989 | 0.0789, | 0.0357, 0.0833 |
| uala) K_1 , WK_2 | 0.1342 | 1 102 and 0 257 | 1 401 and 0 000 | 0.1098 | 0.000 and | 0.1449 | 0.665 and 0.427 |
| peak and hole $(e \text{ Å}^{-3})$ | -0.227 | 1.185 and -0.357 | 1.421 anu -0.986 | -0.157 | -0.323 | -0.240 | 0.005 and -0.427 |

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