

## Putting aniline radical cations in a bottle

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Salts containing aniline radical cations have been isolated and characterized by electron paramagnetic resonance (EPR) spectroscopy, UV-Vis absorption spectroscopy and single crystal X-ray diffraction. The EPR spectra and theoretical calculations indicate the unpaired electron is delocalized on phenyl rings and nitrogen atoms. Both radical cations feature a quinoidal geometry with a partially double C–N bond, but are distinct in that the C–N bond is coplanar to the phenyl plane in one cation while deviates from the plane in the other due to steric crowding. The work provides the first unequivocal examples of stable aniline radical cations.

**aniline radical cations, quinoidal geometry, C–N double bond**

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## 1 Introduction

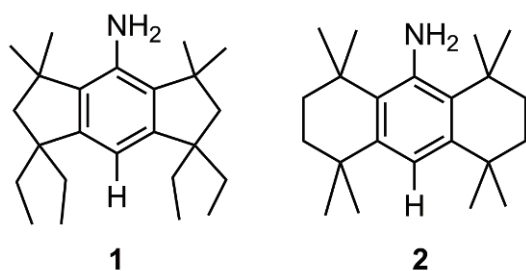
Aniline radical cations ( $\text{ArNR}_2^{+\cdot}$ ,  $\text{R}=\text{H}$  or alkyl) have been the subjects of numerous theoretical, gas-phase and solution experimental studies [1–3]. They are important intermediates occurring in dimerization, cationic polymerization, azo compound formation, benzidine rearrangement, proton transfer reactions, and various nucleophilic substitutions such as nitration, methoxylation, cyanation and halogenation [2–4]. However, aniline radical cations are highly reactive and only short-lived in solution [2a,4b,5]. The 2,4,6-tri-*t*-BuC<sub>6</sub>H<sub>2</sub>NH<sub>2</sub> aniline radical cation was detected in solution [5], but its identity in the solid state recently has been under a debate [6]. Isolation of salts with an aniline radical cation remains a

challenge. By considering the steric effect, electronic property and weakly coordinating anions [7], we now successfully stabilized two aniline radical cations both in solution and the solid states. Their syntheses, characterization and structures are described in this paper.

## 2 Experimental

All experiments were carried out under a nitrogen atmosphere by using standard Schlenk techniques and a glovebox. Solvents were dried prior to use. 1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene (Alfa Aesar, USA) was purchased and used upon arrival. **1** (Scheme 1) [8] and  $\text{Ag}[\text{Al}(\text{OR}_F)_4]$  ( $\text{OR}_F=\text{OC}(\text{CF}_3)_3$ ) [9] were synthesized according to the literature methods. **2** was synthesized by a similar method. Cyclic voltammetry was performed on an IM6ex electrochemical workstation, with platinum as the working and counter electrodes,  $\text{Ag}/\text{Ag}^+$  as the reference ele-

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**Scheme 1** Anilines **1** and **2**.

ctrode and 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. EPR spectra were obtained using Bruker EMX-10/12 variable-temperature apparatus (Germany). UV-Vis spectra were recorded on the Lambda 750 spectrometer (USA). Element analyses were performed at Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were performed using a Bruker DRX-500 spectrometer (Germany) in ppm downfield from Me<sub>4</sub>Si. X-ray crystal structures were obtained by using a Bruker APEX DUO CCD detector (Germany).

## 2.1 Synthesis of **2**

To a mixture of 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene (5.0 g, 16.7 mmol), CH<sub>2</sub>Cl<sub>2</sub> (100 mL), acetic anhydride (60 mL) and acetic acid (50 mL) were added fuming nitric acid (10 mL) at 0 °C over a period of 1 h. The mixture was stirred for an additional hour at 0 °C, and then water and CH<sub>2</sub>Cl<sub>2</sub> were added. The organic layer was separated and washed successively with water, aqueous sodium carbonate and brine. After drying over anhydrous magnesium sulfate, the crude material was filtered and evaporated for the next step. To a vigorously stirred mixture of the above crude product (3.0 g), CH<sub>2</sub>Cl<sub>2</sub> (100 mL), MeOH (50 mL) and nickel(II) chloride hexahydrate (0.50 g, 2.1 mmol) was added sodium borohydride (2.5 g, 66 mmol) portionwise over a period of 1 h at 0 °C. The mixture was stirred for an additional hour and then filtered through a plug of Celite®. The organic layer was separated, and washed successively with water and brine, and dried over anhydrous sodium sulfate. After filtration the solvent was removed in vacuo and the residue was loaded silica gel column and flushed using dichloromethane:hexane (1:3, v/v) as eluent affording the pure **2** as a colorless solid (1.75 g). m.p. 105–108 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.78 (s, 1H), 1.68 (t, 4H), 1.61 (t, 4H), 1.45 (s, 12H), 1.26 (s, 12H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 144.0, 143.6, 126.8, 116.8, 40.4, 35.2, 34.8, 33.7, 32.5, 28.3. Anal. Calcd. for C<sub>22</sub>H<sub>35</sub>N, C, 84.28; H, 11.25; N, 4.47. Found C, 84.18; H, 11.22; N, 4.60.

## 2.2 Preparation of **1**<sup>+</sup>[Al(OR<sub>F</sub>)<sub>4</sub>]<sup>-</sup>

Under anaerobic and anhydrous conditions, a mix-

ture of **1** (0.068 g, 0.20 mmol) and Ag[Al(OR<sub>F</sub>)<sub>4</sub>] (0.22 g, 0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (~50 mL) was stirred at room temperature for 1 d. The resultant brownish yellow solution was filtered to remove the gray precipitate (Ag metal). The solvent was removed from the solution under reduced pressure. The crude oil was washed by small amounts of hexane and it gradually became solid powder. After filtration, the resulting crude solid was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, then concentrated and stored at around -20 °C for 24 h to afford X-ray-quality crystals of the radical cation salt **1**<sup>+</sup>[Al(OR<sub>F</sub>)<sub>4</sub>]<sup>-</sup>. Isolated yield: 0.11 g, 45% (crystals); m.p. 95–97 °C (decomp.); UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>=493 nm (ε 24870), 1163 (ε 1128). Elemental analysis calcd. (%) for C<sub>40</sub>H<sub>39</sub>AlF<sub>36</sub>NO<sub>4</sub>: C 36.71, H 3.00, N 1.07; Found: C 37.66, H 3.38, N 0.89.

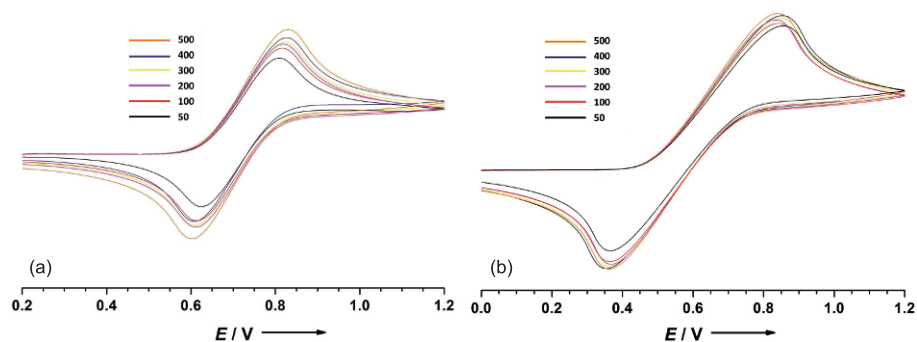
## 2.3 Preparation of **2**<sup>+</sup>[Al(OR<sub>F</sub>)<sub>4</sub>]<sup>-</sup>

Under anaerobic and anhydrous conditions, a mixture of **2** (0.078 g, 0.20 mmol) and Ag [Al(OR<sub>F</sub>)<sub>4</sub>] (0.22 g, 0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (~50 mL) was stirred at room temperature for 1 d. The resultant yellow solution was filtered to remove the gray precipitate (Ag metal). The solvent was removed from the solution under reduced pressure. The crude oil was washed by small amounts of hexane and it gradually became yellow solid powder. After filtration, the resulting crude solid was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, then concentrated and stored at around -20 °C for 24 h to afford crystals of the radical cation salt **2**<sup>+</sup>[Al(OR<sub>F</sub>)<sub>4</sub>]<sup>-</sup>. Isolated yield: 0.12 g, 46% (crystals); m.p. 110–112 °C (decomp.); UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>=464 nm (ε 7450), 936 nm (ε 350). Elemental analysis calcd. (%) for C<sub>38</sub>H<sub>35</sub>AlF<sub>36</sub>NO<sub>4</sub>: C 35.64, H 2.75, N 1.09; Found: C 36.48, H 3.13, N 0.85.

## 3 Results and discussion

Cyclic voltammetry (CV) of **1** and **2** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature with Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte reveals reversible oxidation peaks (Figure 1), indicating that the radical cations **1**<sup>+</sup> and **2**<sup>+</sup> are persistent under these conditions. Prompted by these CV data, **1** and **2** were treated with 1 equiv. of Ag[Al(OR<sub>F</sub>)<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> to afford colored solutions of radical cations **1**<sup>+</sup> and **2**<sup>+</sup>, which were isolated as brown and yellow crystals, respectively. Radical cation salts were obtained upon workup in considerable yields and are stable under nitrogen or argon atmosphere at room temperature. The highly stable nature of **1**<sup>+</sup> and **2**<sup>+</sup> is most likely attributed to the steric bulkiness of the supporting ligands and the weakly coordinating anion [Al(OR<sub>F</sub>)<sub>4</sub>]<sup>-</sup>.

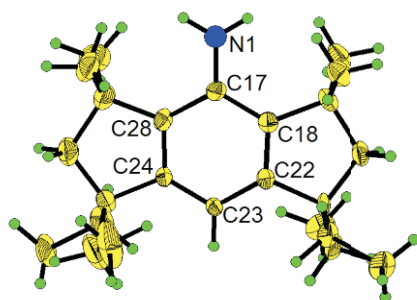
Crystals for X-ray crystallographic studies were obtained by cooling solutions of salts **1**<sup>+</sup> and **2**<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> [10]. For comparison, we also obtained the colorless crystals of precursor **1** from methanol and determined its structure. **1**<sup>+</sup>[Al(OR<sub>F</sub>)<sub>4</sub>]<sup>-</sup> crystallizes in the monoclinic space group



**Figure 1** Cyclic voltammograms of **1** (a) and **2** (b) in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-4}$  M, 0.1 M *n*- $\text{Bu}_4\text{NPF}_6$ , 298 K) measured at various scans: 50, 100, 200, 300, 400, and 500 mV/s (color online).

$P2(1)$ , and the hydrogen atoms attached to nitrogen were directly found in the difference maps and refined freely. The crystal contains three independent radical cations of  $\mathbf{1}^{+\bullet}$  with similar geometries, one of which is shown as a stereoview in Figure 2. The nearest intermolecular  $\text{N} \cdots \text{N}$  distance is 11.588 Å, suggesting no intermolecular interaction presence in  $\mathbf{1}^{+\bullet}$ . A list of important structural parameters as average of three geometries, along with those of the neutral molecule **1**, is given in Table 1. The C17–N1 bond of  $\mathbf{1}^{+\bullet}$  is coplanar to the phenyl ring with its length shorter by 0.08 Å than that of **1**. The longitudinal bond (*c*) inside the ring is contracted while the transverse bonds (*b* and *d*) are elongated, leading to a quinoid-type structure. The crystal structure of  $\mathbf{2}^{+\bullet}[\text{Al}(\text{OR}_f)_4]^-$  is extremely disordered and cannot be fully solved. As a result, the phenyl C–C bond lengths were only solved as averaged values. However, it can be clearly seen that the C–N bond deviates from the phenyl plane (Figure S1 in the Supporting Information online) in  $\mathbf{2}^{+\bullet}$ , distinct from the planar geometry of  $\mathbf{1}^{+\bullet}$ .

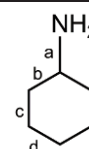
To rationalize the experimental results and get further insights into their electronic structures, we carried out calculations for species  $\mathbf{1}^{+\bullet}$  and  $\mathbf{2}^{+\bullet}$ , along with parent molecules **1** and **2** at the level of (U)BH&HLYP/6-31G(d) [11]. The calculated structural parameters of  $\mathbf{1}^{+\bullet}$  agree well with those of the X-ray crystal structure (Table 1). Consistent with the experimental data, calculations give a quinoid-type structure



**Figure 2** Thermal ellipsoid (50%) drawing of the crystal structure of  $\mathbf{1}^{+\bullet}$ . Yellow C; green H; blue N (color online).

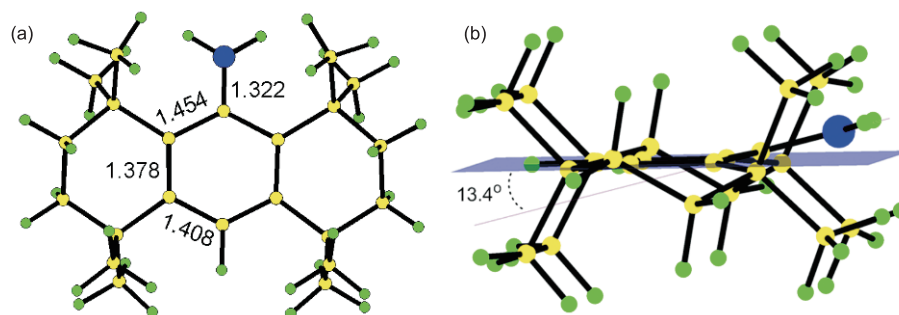
**Table 1** Selected experimental and calculated structural parameters (Å, avg) of **1** and  $\mathbf{1}^{+\bullet}$

	<b>1</b>		$\mathbf{1}^{+\bullet}$	
	EXP	DFT	EXP	DFT
a	1.407(3)	1.396	1.324(5)	1.323
b	1.404(3)	1.401	1.440(5)	1.438
c	1.498(3)	1.388	1.365(5)	1.368
d	1.391(3)	1.384	1.406(5)	1.406

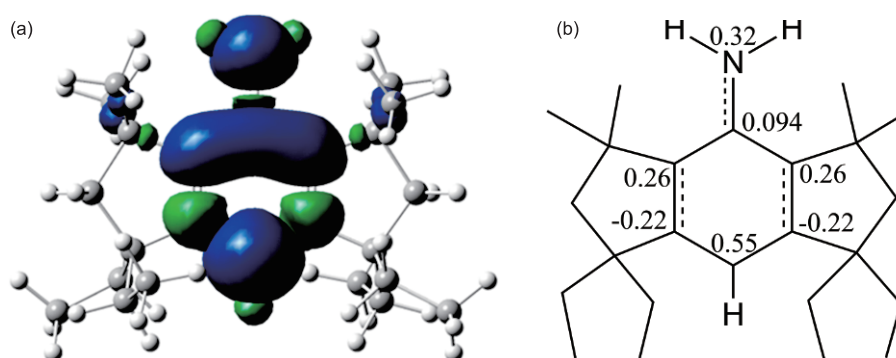


with a partial double C–N bond for both cations. Of particular note, the calculated geometry of  $\mathbf{2}^{+\bullet}$  (Figure 3) shows a dihedral angle of 13.4° between the C–N bond and the phenyl plane, comparable to the preliminary crystal structure of  $\mathbf{2}^{+\bullet}$  (Figure S1). The calculation shows only 21% of the total unpaired spin density of  $\mathbf{1}^{+\bullet}$  residing on the nitrogen (0.32). The remainder is largely delocalized on the *para*-carbon (C23, 0.55%, 35%) and the *ortho*-carbon atoms (C18 and C28, 0.26% avg, 34%), as shown in Figure 4. Negative spin densities are found at the *meta*-carbon (C22 and 24, –0.22 avg) positions. A similar spin density distribution was computed for  $\mathbf{2}^{+\bullet}$  (Figure S2). Bond lengths and the calculated spin density distributions indicate the aniline radical cations are stabilized by resonance structures shown in Scheme 2 (for  $\mathbf{1}^{+\bullet}$ ).

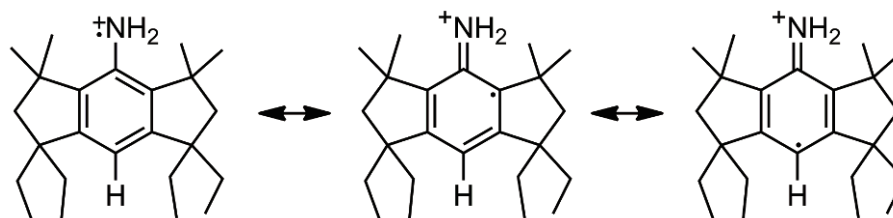
The simulated EPR spectra are in good agreement with the experimental EPR spectra (Figure 5(a) for  $\mathbf{1}^{+\bullet}$ , For  $\mathbf{2}^{+\bullet}$  see Figure S3) revealing a pattern coupling with H and N atoms ( $\mathbf{1}^{+\bullet}$   $g=2.0028$ ,  $a_{\text{N}}=6.30$  G,  $a_{\text{H}}^{\text{NH}}=7.77$  G (2H),  $a_{\text{H}}^{\text{phenyl}}=9.55$  G (1H);  $\mathbf{2}^{+\bullet}$   $g=2.0028$ ,  $a_{\text{N}}=6.36$  G,  $a_{\text{H}}^{\text{NH}}=6.62$  G (2H),  $a_{\text{H}}^{\text{phenyl}}=9.60$  G (1H)). The  $g$  factors are in the range of 2.0027–2.0029 for reported but unstable alkylsubstituted aniline radical cations [12]. The coupling constants ( $a_{\text{N}}$  and  $a_{\text{H}}^{\text{NH}}$ ) are similar to those for the EPR spectrum of 2,4,6-tri-*t*-BuC<sub>6</sub>H<sub>2</sub>NH<sub>2</sub> aniline radical cation in solution [5], while the coupling constants ( $a_{\text{H}}^{\text{phenyl}}$ ) are in



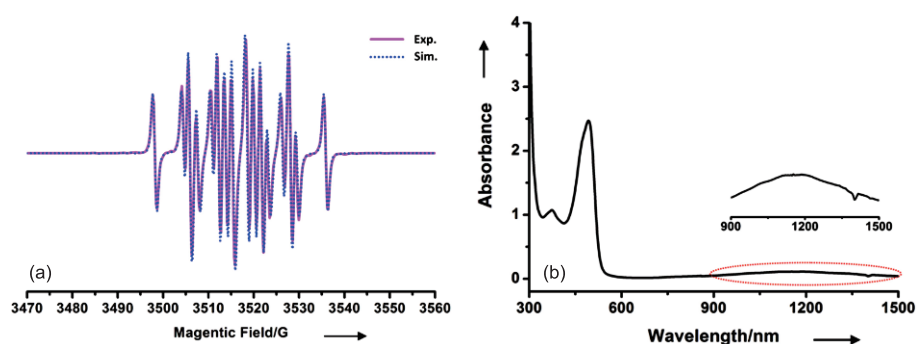
**Figure 3** Calculated geometries of  $2^{+}$  at the level of UBH&HLYP/6-31G(d) with side and top views (bond length: Å). Yellow C; green H; blue N (color online).



**Figure 4** Electron spin density distribution of  $1^{+}$  (color online).



**Scheme 2** Resonance structures of  $1^{+}$ .



**Figure 5** (a) Experimental (pink solid lines) and simulated (blue dot lines) EPR spectra for  $1 \times 10^{-3}$  M  $\text{CH}_2\text{Cl}_2$  solution of  $1^{+}[\text{Al}(\text{OR}_f)_4]^{-}$  (298 K); (b) absorption spectrum of  $1^{+}$  in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-4}$  M, 298 K) (color online).

sharp contrast to those resulted from the coupling with *meta*-carbon atoms in 2,4,6-tri-*t*-BuC<sub>6</sub>H<sub>2</sub>NH<sub>2</sub> aniline radical cation, indicating substantial amounts of the unpaired electron residing on the *para*-carbon atoms in the current radical cations, which is consistent with calculated spin density

distributions. The absorption spectrum of  $1^{+}$  (Figure 5(b)) in  $\text{CH}_2\text{Cl}_2$  shows main bands around 470 and 1100 nm ( $2^{+}$ : 470, 950 nm, Figure S6). TD-DFT calculations at the UB3LYP/6-31G(d) level indicate these peaks are mainly due to HOMO( $\beta$ ) $\rightarrow$ LUMO( $\beta$ ), HOMO-1( $\beta$ ) $\rightarrow$ LUMO( $\beta$ ) and

HOMO-2( $\beta$ ) $\rightarrow$ LUMO( $\beta$ ) electronic transitions (Figures S7 and S8).

## 4 Conclusions

We herein have described the stabilization and characterization of two aniline radical cations  $1^{+\bullet}$  and  $2^{+\bullet}$ . The EPR spectra and theoretical calculations indicate the unpaired electron is delocalized on phenyl ring and nitrogen atom. Both radical cations feature a quinoidal geometry with a short C–N bond, but differently the C–N bond is coplanar to the phenyl plane in  $1^{+\bullet}$  while deviates from that in  $2^{+\bullet}$  due to steric crowding. The work thus provides the first unequivocal examples of stable aniline radical cations. The isolation and structural studies of such radical species may have impact on the fields of radical chemistry and organic reactions. Further studies on the chemical reactivity of these newly synthesized aniline radicals are under way.

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**Conflict of interest** The authors declare that they have no conflict of interest.

**Supporting information** The supporting information is available online at <http://chem.scichina.com> and <http://link.springer.com/journal/11426>. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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- X-ray data for **1** and  $1^{+\bullet}[\text{Al}(\text{ORF})_4]^-$  (MoK $\alpha$ ,  $\lambda=0.71073$  Å): **1** C<sub>24</sub>H<sub>39</sub>N, FW=341.56, triclinic, space group *P*-1, *Z*=2,  $\mu=0.062$  mm<sup>-1</sup>,  $a=9.316(4)$ ,  $b=9.906(4)$ ,  $c=12.232(5)$  Å,  $\alpha=89.325(6)^\circ$ ,  $\beta=70.241(6)^\circ$ ,  $\gamma=76.382(6)^\circ$ ,  $T=123(2)$  K,  $V=1029.7(7)$  Å<sup>3</sup>,  $R1=0.0762$  ( $I>2\sigma(I)$ ),  $wR2=0.1872$  (all data).  $1^{+\bullet}[\text{Al}(\text{ORF})_4]^-$  C<sub>40</sub>H<sub>39</sub>AlF<sub>36</sub>NO<sub>4</sub>, FW=1308.70, monoclinic, spacegroup *P*2(1), *Z*=6,  $\mu=0.214$  mm<sup>-1</sup>,  $a=11.0117(10)$ ,  $b=21.4263(19)$ ,  $c=32.292(3)$  Å,  $\beta=91.158(2)^\circ$ ,  $T=123(2)$  K,  $V=7617.3(12)$  Å<sup>3</sup>,  $R1=0.0540$  ( $I>2\sigma(I)$ ),  $wR2=0.1185$  (all data). CCDC-1063400-1063401 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/Data\\_request/cif](http://www.ccdc.cam.ac.uk/Data_request/cif)
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