

# Sandwich-Type Heteroleptic *opposite*-(Diazaporphyrinato)cerium Complexes: Synthesis, Spectroscopy, Structure, and Electrochemistry

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Two sandwich-type heteroleptic tetrapyrrole cerium complexes,  $\text{Ce}_2(\text{dap})_2(\text{pc})$  (**1**) [ $\text{dap}$  = 2,8,12,18-tetraethyl-3,7-13,17-tetramethyl-5,15-diazaporphyrinate;  $\text{pc}$  = phthalocyaninate] and  $\text{Ce}(\text{dap})(\text{oep})$  (**2**) ( $\text{oep}$  = octaethylporphyrinate), were prepared by a one-pot reaction of  $[\text{Ce}(\text{acac})_3] \cdot n\text{H}_2\text{O}$  ( $\text{acac}$  = acetylacetonate), metal-free diazaporphyrin  $\text{H}_2\text{dap}$ , and  $\text{Li}_2\text{pc}$  or  $\text{H}_2\text{oep}$  in refluxing 1,2,4-trichlorobenzene. These sandwich double- and triple-decker complexes were characterized by a wide range of spectroscopic methods in

addition to elemental analysis. Their electrochemistry was also studied by cyclic voltammetry and differential pulse voltammetry. The molecular structure of  $\text{Ce}_2(\text{dap})_2(\text{pc})$  (**1**) was determined by X-ray diffraction analysis, indicating an unexpected asymmetrical disposition of the ligands, with two adjacent  $\text{dap}$  moieties and one outer  $\text{pc}$  ring.

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## Introduction

As one of the most important tetrapyrrole derivatives, phthalocyanines have been an important class of dyes and pigments due to their wide range of applications in catalysts, deodorants, and molecular electronics.<sup>[1]</sup> The biology and chemistry of naturally occurring porphyrins have also been intensively studied. Particularly, many artificial porphyrin derivatives have been prepared and characterized in the last 30 years.<sup>[2]</sup> As the median in structure and composition between the phthalocyanine and porphyrin compounds, *opposite*-diazaporphyrine with  $D_{2h}$  symmetry for its dianion was first reported in 1935 and has been introduced into several metal complexes thereafter.<sup>[3,4]</sup> However, sandwich-type, tetrapyrrole, rare-earth complexes containing *opposite*-diazaporphyrinato ligands are still very scarce, and to the best of our knowledge, this class of compounds is limited to the sole example of homoleptic triple-decker complexes  $\text{M}_2(\text{dap})_3$  ( $\text{M}$  = Eu, Ce), reported by this group recently.<sup>[5]</sup>

It is worth noting that sandwich-type tetrapyrrole rare-earth complexes with porphyrinato and phthalocyaninato ligands (with  $D_{4h}$  symmetry for its dianion) have been intensively and extensively studied in the past several decades.<sup>[6]</sup> It has also been revealed that the electronic structure and spectroscopic properties of sandwich-type rare-earth compounds are affected significantly by the reduction in molecular symmetry of the tetrapyrrole ligands used.<sup>[5,7]</sup> To enhance the understanding of the electronic structure and spectroscopic properties of sandwich-type tetrapyrrole complexes, as mentioned above we reported the synthesis and characterization of the first homoleptic, *opposite*-diazaporphyrinato, rare-earth, triple-decker complexes.<sup>[5]</sup> In the present work, we extend our efforts in this regard and describe the synthesis, spectroscopy, electrochemistry, and molecular structure of two heteroleptic cerium sandwich compounds,  $\text{Ce}_2(\text{dap})_2(\text{pc})$  (**1**) and  $\text{Ce}(\text{dap})(\text{oep})$  (**2**), each of which contains two kinds of tetrapyrrole ligands with quite different electronic properties (Figure 1).

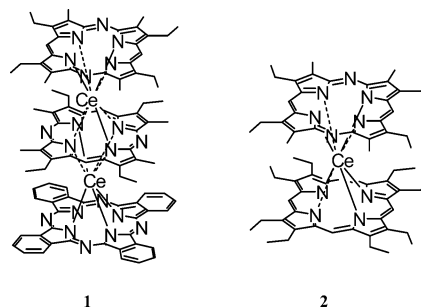


Figure 1. Schematic structure of cerium triple-decker  $\text{Ce}_2(\text{dap})_2(\text{pc})$  (**1**) and double-decker  $\text{Ce}(\text{dap})(\text{oep})$  (**2**) complexes.

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## Results and Discussion

### Synthesis of $\text{Ce}_2(\text{dap})_2(\text{pc})$ (**1**) and $\text{Ce}(\text{dap})(\text{oep})$ (**2**)

By employing the synthetic pathway used to prepare mixed (phthalocyaninato)(porphyrinato) rare-earth complexes, heteroleptic tetrapyrrole cerium complexes containing *opposite*-diazaporphyrinato ligand(s) **1** and **2** were synthesized.<sup>[2d,6c]</sup> Treatment of  $[\text{Ce}(\text{acac})_3] \cdot n\text{H}_2\text{O}$ , metal-free diazaporphyrin  $\text{H}_2\text{dap}$ , and  $\text{Li}_2\text{pc}$  or  $\text{H}_2(\text{oep})$  in refluxing 1,2,4-trichlorobenzene (tcb) gave a mixture containing different kinds of sandwich-type products, from which the target triple-decker  $\text{Ce}_2(\text{dap})_2(\text{pc})$  (**1**) and double-decker  $\text{Ce}(\text{dap})(\text{oep})$  (**2**) could be easily separated by general column chromatography. It is worth noting that in preparing triple-decker  $\text{Ce}_2(\text{dap})_2(\text{pc})$  (**1**) attempts to increase the yield of the target compound by increasing the reaction time to more than 16 h led to the production of quite a large fraction of the homoleptic triple-decker  $\text{Ce}_2(\text{dap})_3$ .

### Electronic Absorption and Magnetic Circular Dichroism Spectroscopy

The electronic absorption spectra of **1** and **2** in  $\text{CHCl}_3$  are shown in Figure 2. As can be seen, both heteroleptic complexes **1** and **2** display only a single but broad B band. This is in contrast to the clearly split two B bands observed in the mixed (phthalocyaninato)(porphyrinato) rare-earth complexes  $\text{M}_2(\text{por}')_2(\text{pc})$  and  $\text{M}(\text{por})(\text{pc})$  (por = ttyp, tpp, tclpp, tompp, tbpp), which are mainly attributed to individual macrocycles, respectively.<sup>[10–13]</sup> On the basis of observation of only one B band in the heteroleptic bis- and tris(por-

phyrinato) or bis- and tris(phthalocyaninato) metal complexes containing two or three different porphyrinato or phthalocyaninato ligands,<sup>[8,9]</sup> the fact that only one B band is observed in the electronic absorption spectra of sandwich-type complexes **1** and **2** clearly demonstrates the closeness in electronic structure and spectroscopic properties between *opposite*-diazaporphyrine and porphyrin and between *opposite*-diazaporphyrine and phthalocyanine. In other words, *opposite*-diazaporphyrine is located as the median between porphyrin and phthalocyanine in electronic structure and electronic absorption properties.

The magnetic circular dichroism (MCD) spectra of **1** and **2** in  $\text{CHCl}_3$  are also shown in Figure 2. The MCD spectra of **1** and **2** are all Faraday *B*-terms theoretically, whereas Faraday *A*-term-like MCD curves were obtained in the region of the Q and B bands due to the superimposition of closely lying *B*-terms of opposite sign, although the constituting  $\text{H}_2\text{dap}$  shows MCD peaks and troughs associated with absorption peaks and shoulders (Faraday *B*-terms).<sup>[3c]</sup> For example, in the MCD spectrum of **2**, one dispersion-type curve in the B band region appears between ca. 331 and 357 nm and is associated with an absorption peak at 358 nm, and the other one lies between ca. 565 and 686 nm in the Q-band region corresponding to the absorption peak at 583 nm. The B-band is significantly blueshifted compared to that of  $\text{Ce}(\text{oep})_2$ ,<sup>[14]</sup> whereas the Q-band is redshifted.<sup>[4]</sup> Similar spectroscopic shifts were observed previously between  $D_{2h}$ -type monomer species and the corresponding homoleptic triple-decker complexes.<sup>[3c,5]</sup>

### Electrochemical Properties

The electrochemical properties of compounds **1** and **2** were investigated through cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dry dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). These sandwich-type complexes displayed several one-electron oxidation and one-electron reduction processes within the electrochemical window of  $\text{CH}_2\text{Cl}_2$ . The half-wave redox potentials are summarized in Table 1. As shown in the cyclic and differential pulse voltammograms of **2** (Figure 3), in addition to three reversible ring-based oxidations and two reversible ring-based reductions, an irreversible reduction wave at  $-0.87$  V vs. SCE due to the  $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$  process is also observed. Such an irreversible reduction has also been observed for sandwich-type cerium complexes of porphyrin and phthalocyanine.<sup>[12a,15]</sup> As reported previously, the first oxidation process of  $\text{Ce}(\text{oep})(\text{TPP})$  at  $0.402$  V vs. SCE, lower in comparison to that of  $\text{Ce}(\text{TPP})_2$ , is attributed to the lower oxidation potential of the oep ligand.<sup>[3c,16]</sup> In line with this observation, the smaller value of the first oxidation observed for **2** at  $0.35$  V

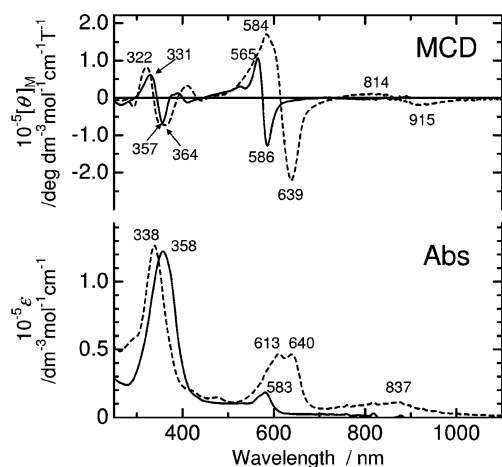


Figure 2. MCD (top) and electronic absorption spectra (bottom) of  $[\text{Ce}_2(\text{dap})_2(\text{pc})]$  (**1**) (broken lines) and  $\text{Ce}(\text{dap})(\text{oep})$  (**2**) (solid lines) in  $\text{CHCl}_3$ .

Table 1. Half-wave redox potentials (V vs. SCE) for  $[\text{Ce}_2(\text{dap})_2(\text{pc})]$  (**1**) and  $\text{Ce}(\text{dap})(\text{oep})$  (**2**) in  $\text{CH}_2\text{Cl}_2$  containing  $0.1$  M TBAP.

	O <sub>5</sub>	O <sub>4</sub>	O <sub>3</sub>	O <sub>2</sub>	O <sub>1</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>
<b>1</b> <sup>[a]</sup>	1.31	1.07	0.87	0.65	0.50	−0.81	−0.91	−1.11	−1.28	−1.61
<b>2</b>			1.90 <sup>[a]</sup>	0.91	0.35	−0.51	−0.87	−1.72 <sup>[a]</sup>		

[a] Data from differential pulse voltammogram.

should also be due to the greater contribution from the oep ring in this complex. This also corresponds well with the redshift observed for the lowest-energy  $\pi$ - $\pi^*$  bands of **2**.

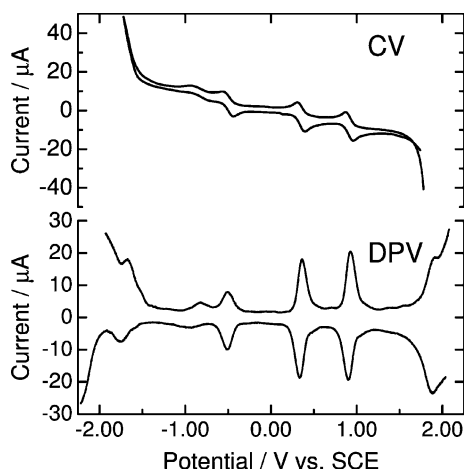


Figure 3. (a) Cyclic voltammogram (top) and differential pulse voltammogram (bottom) of Ce(dap)(oep) (**2**) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M [NBu<sub>4</sub>][ClO<sub>4</sub>] at a scan rate of 20 and 10 mV s<sup>-1</sup>, respectively.

### Structure Studies

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol into a toluene solution of this compound. This compound crystallizes in the orthorhombic system with a *Pna*2<sub>1</sub> space group with four molecules in one unit cell (Table 2). The molecular structure of **1** in two different perspective views is shown in Figure 4. It can be seen that the two cerium centers are not identical in terms of their coordination environments. One is octacoordinated by the eight pyrrole nitrogen atoms from

the outer dap and medium dap ligands, whereas the other is coordinated by four pyrrole nitrogen atoms from the medium dap ligand and another four isoindole nitrogen atoms of the outer pc ring, indicating the asymmetrical structure in the form of (dap)Ce(dap)Ce(pc) in the triple-decker molecule. The Ce–Ce distance is 3.679 Å; both cerium centers lie closer to the outer dap and pc rings (1.478 vs. 1.781 Å for Ce1; 1.395 vs. 1.899 Å for Ce2). The external and internal dap ligands rotate by ca. 45° with respect to the Ce–N<sub>meso</sub> vectors. These structural features are obviously different from those revealed in the mixed [(na)-phthalocyaninato](porphyrinato) rare-earth triple-decker analogues, such as [Ce<sub>2</sub>{pc(OMe)<sub>8</sub>}(tpp)<sub>2</sub>] [pc(OMe)<sub>8</sub> = 2,3,9,10,16,17,23,24-octamethoxyphthalocyaninate; tpp = *meso*-tetraphenylporphyrinate],<sup>[17]</sup> [(tpp)Ce(pc)Gd(oep)],<sup>[18]</sup> and [Nd<sub>2</sub>(nc)(oep)<sub>2</sub>] (nc = naphthalocyaninate).<sup>[19]</sup>

[M<sub>2</sub>(pc)(tclpp)<sub>2</sub>] (M = Y, Ho),<sup>[10c]</sup> in which the substituted or unsubstituted (na)phthalocyanine ring lies between two porphyrin rings to yield a symmetrical molecular structure for these mixed-ring, sandwich-type, triple-decker compounds. This reveals that differences in the molecular and electronic structures still exist between the porphyrinato and *opposite*-diazaporphyrinato ligands due to the replacement of two *meso*-CH fractions by nitrogen atoms in the latter ligand.

### Conclusion

We prepared two heteroleptic sandwich-type cerium complexes containing *opposite*-diazaporphyrinato ligands with *D*<sub>2h</sub> symmetry, one with a triple-decker structure and the other with a double-decker structure. The molecular structure of Ce<sub>2</sub>(dap)<sub>2</sub>(pc) was verified by X-ray crystallography, revealing its asymmetrical molecular structure in

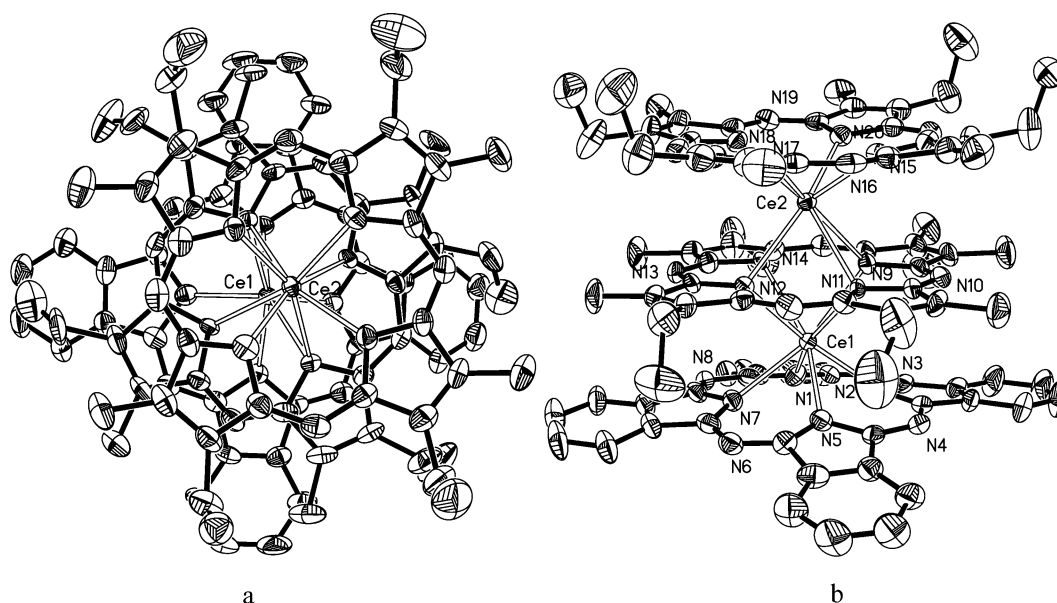


Figure 4. Molecular structure of [Ce<sub>2</sub>(dap)<sub>2</sub>(pc)] (**1**) in two perspective views: (a) top view and (b) side view. Hydrogen atoms are omitted for clarity and the ellipsoids are drawn at the 30% probability level.

the form of (dap)Ce(dap)Ce(pc). Electrochemical and spectroscopic investigation provided information on the differences between sandwich-type, tetrapyrrole, rare-earth complexes containing the diazaporphyrinato ligand and the extensively studied porphyrinato and phthalocyaninato analogues.

## Experimental Section

**General Remarks:** [Ce(acac)<sub>3</sub>] $\cdot$ *n*H<sub>2</sub>O,<sup>[20]</sup> H<sub>2</sub>dap,<sup>[21]</sup> and Li<sub>2</sub>pc<sup>[22]</sup> were prepared according to literature procedures. H<sub>2</sub>oep (Aldrich) and anhydrous tcb (Aldrich) were used as commercially supplied. Details regarding the treatment of the other solvents have been described previously.<sup>[13c]</sup> Mass spectra were obtained with a Bruker BIFLEX III ultra-high-resolution mass spectrometer (MALDI-TOF). Electronic absorption spectra were recorded with a Hitachi U-3410 spectrophotometer by using chloroform as the solvent. Magnetic circular dichroism (MCD) measurements were made with a JASCO J-725 spectrophotometer equipped with a JASCO electromagnet that produces magnetic fields up to 1.09 T. Its magnitude was expressed in terms of molar ellipticity per tesla, [ $\theta$ ]<sub>M</sub>/° mol<sup>-1</sup> L cm<sup>-1</sup> T<sup>-1</sup>. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode with a diameter of 2.0 mm and a silver-wire counter electrode. The reference electrode was Ag/Ag<sup>+</sup>, which was connected to the solution by a luggin capillary, whose tip was placed close to the working electrode, corrected for junction potential by being referenced internally to the ferrocenium/ferrocene (Fe<sup>+</sup>/Fe) couple [ $E_{1/2}$ (Fe<sup>+</sup>/Fe) = 501 mV vs. SCE]. Typically, a 0.1 M solution of [Bu<sub>4</sub>N][ClO<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> containing 0.5 mM of sample was purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rates were 20 and 10 mV s<sup>-1</sup> for CV and DPV, respectively.

**Ce<sub>2</sub>(dap)<sub>2</sub>(pc) (1):** A mixture of [Ce(acac)<sub>3</sub>] $\cdot$ *n*H<sub>2</sub>O (30 mg, 0.04 mmol), Li<sub>2</sub>pc (16 mg, 0.03 mmol), and H<sub>2</sub>dap (10 mg, 0.02 mmol) in tcb (4 mL) was heated to reflux under a nitrogen atmosphere for 8 h. The mixture was cooled briefly, and the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column by using CHCl<sub>3</sub> as the eluent to give **1** (5.6 mg, 32%).  $R_f$  = 0.60. MS (MALDI-TOF):  $m/z$  = 1749.5 [M]<sup>+</sup>. UV/Vis (CHCl<sub>3</sub>):  $\lambda$  = 338, 474, 613, 640, 837 nm. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.43 (s, 8 H, H<sub>oep</sub>), 4.72 (s, 8 H, H<sub>pc</sub>) 1.59 (s, 20 H, CH<sub>2</sub>CH<sub>3</sub>-dap), 0.39–1.29 (12 H, -CH<sub>3</sub>-dap) ppm. C<sub>92</sub>H<sub>84</sub>N<sub>20</sub>Ce<sub>2</sub>·2H<sub>2</sub>O: (1786.02) calcd. C 61.87, H 4.97, N 15.68; found C 61.78, H 4.58, N 15.36.

**Ce(dap)(oep) (2):** A mixture of [Ce(acac)<sub>3</sub>] $\cdot$ *n*H<sub>2</sub>O (393 mg, 0.9 mmol), H<sub>2</sub>(oep) (78 mg, 0.15 mmol), and H<sub>2</sub>dap (70 mg, 0.15 mmol) in tcb (4 mL) was heated at reflux overnight (18 h) under a nitrogen atmosphere to give **2** (25.8 mg, 15%) after alumina column chromatography by using toluene as the eluent.  $R_f$  = 0.65. MS (ESI-TOF):  $m/z$  = 1150.95 [M]<sup>+</sup>. UV/Vis (CHCl<sub>3</sub>):  $\lambda$  = 359.7, 581.1 nm. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.53–1.77 (m, 36 H, -CH<sub>3</sub> from oep and dap), 2.95–3.18 (m, 12 H, -CH<sub>3</sub>-tap), 3.29–3.58 (m, 16 H, -CH<sub>2</sub>-oep), 3.78–3.88 (m, 8 H, -CH<sub>2</sub>-dap), 8.74 (s, 2 H, *meso*, H-dap), 8.97 (s, 4 H, *meso*, H-oep) ppm.

**X-ray Crystallography:** Crystal data were collected with a Bruker SMART CCD diffractometer with an Mo- $K_\alpha$  sealed tube ( $\lambda$  = 0.71073 Å) at 293 K by using the  $\omega$ -scan mode with an increment of 0.3°. Preliminary unit-cell parameters were obtained from 45 frames. Final unit-cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data.

The collected frames were integrated by using the preliminary cell-orientation matrix. SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling;<sup>[23]</sup> SADABS for absorption correction;<sup>[24]</sup> and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.<sup>[25]</sup> The crystallographic data for **1** is presented in Table 2. CCDC-703440 (for **1**) contains 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).

Table 2. Crystallographic data for [Ce<sub>2</sub>(dap)<sub>2</sub>(pc)](**1**).

	<b>1</b>
Formula	C <sub>92</sub> H <sub>84</sub> Ce <sub>2</sub> N <sub>20</sub>
$M_r$	1750.03
Crystal size / mm <sup>3</sup>	0.55 × 0.42 × 0.05
Crystal system	orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>
$a$ / Å	17.332(13)
$b$ / Å	17.691(13)
$c$ / Å	26.83(2)
$\beta$ / °	90
$V$ / Å <sup>3</sup>	8227(10)
$Z$	4
$\mu$	1.152
Reflections collected	40041
Independent reflections	14299
$R_{int}$	0.0587
$R_1$ [ $I > 2\sigma(I)$ ]	0.0444
$wR_2$ [ $I > 2\sigma(I)$ ]	0.0905
Goodness of fit	1.071

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