

## Solution-Behavior of Ionic Palladium(II) Complexes Sensitive to Metallophilicity of Counteranions

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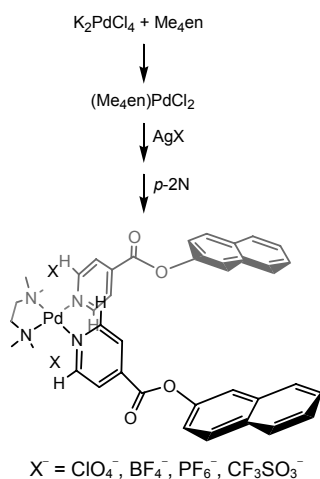
**Key Words:** Counteranion-recognition, Hoffmeister series, Metallophilicity, Palladium(II) complexes

Some palladium(II) complexes of *N*-donor ligands have been synthesized for catalysts,<sup>1</sup> rectangle building blocks,<sup>2</sup> submicrospheres,<sup>3</sup> task-specific morphology,<sup>4</sup> hydrogelation,<sup>5</sup> recognition,<sup>6</sup> and magic rings with associative/dissociative dual character of Pd-N bond.<sup>2</sup> Notably, such palladium(II) complexes have been known to be relatively susceptible to chemical triggers.<sup>7,8</sup> The chemistry on some polyatomic anions such as nitrate, triflate, perchlorate, and hexafluorophosphate, the anionic balancers for the cationic skeleton, has become a rapidly emerging field owing to a timely interest from environmental pollution, industrial chemical process, ionic liquids, catalysis, lithium battery, disease pathways, and health-related perspectives.<sup>9-16</sup> A coordinating series of polyatomic anions can be used to quantitatively predict and synthesize the desirable structures.<sup>17-19</sup> More recent developments include exciting advances in anion template assembly, ion-pair recognition, and the function of anions in supramolecular chemistry.<sup>16-19</sup> The features of polyatomic anions such as negative charge, size, a wide range of geometries, significant solvent effects, and pH dependence imply that the anions play crucial roles in the molecular construction.<sup>20-22</sup> Thus, in order to recognize polyatomic anions, metal coordination receptors can be specifically designed according to the selection of basic components such as the coordination geometry of the metal ions, the binding site of the donating atoms, the reactivity, the charge, and the length of the spacer.<sup>10,23</sup> Recently, unusual anionic effects of metallacyclic palladium(II) complexes containing 1,3-bis(3-pyridyl)tetramethyldisiloxane

(*m*-ptms) have been published.<sup>6</sup> In this context, in order to investigate and expand the solution-behaviors of ionic non-metallacyclic palladium(II) complexes depending on counter ions, the sensitive behavior of new palladium(II) analogues containing 2-naphthalenyl isonicotinate (*p*-2N) was carried out.

The reaction of (Me<sub>4</sub>en)Pd(X)<sub>2</sub> (Me<sub>4</sub>en = *N,N,N',N'*-tetramethylethylenediamine; X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) with *p*-2N ligand in a mixture of water and acetone at room temperature produced a discrete ionic species, [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](X)<sub>2</sub> in high yield (Scheme 1). The reaction was carried out in the 1 : 2 mole ratio of *cis*-protected (Me<sub>4</sub>en)Pd(X)<sub>2</sub> and *p*-2N ligand. All products were obtained as stable solids which were soluble in acetonitrile, dimethyl sulfoxide, *N,N*-dimethylformamide, and nitromethane, but were slightly soluble in water, acetone, methanol, and ethanol. Elemental analyses, IR and <sup>1</sup>H NMR spectra were consistent with the proposed structures. IR frequencies of the ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> appeared at 1093, 1061, 841, and 1281 cm<sup>-1</sup>, respectively (Supporting Information).

The crystal structure of [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·Me<sub>2</sub>CO (Table 1) was solved, and the selected bond lengths and angles were listed in Table 2. The crystal structure depicted in Figure 1 indicates that the local geometry around the palladium(II) ion approximates to a typical square planar arrangement with Me<sub>4</sub>en in the essential *cis* position (Pd-N(1) = 2.336(3) Å, Pd-N(2) = 2.231(3) Å; N(1)-Pd-N(2) = 86.1(1)°). The two *p*-2N ligands are coordinated to a palladium(II) ion in a *cis* position (Pd-N(3) =



**Scheme 1.** Synthetic procedure

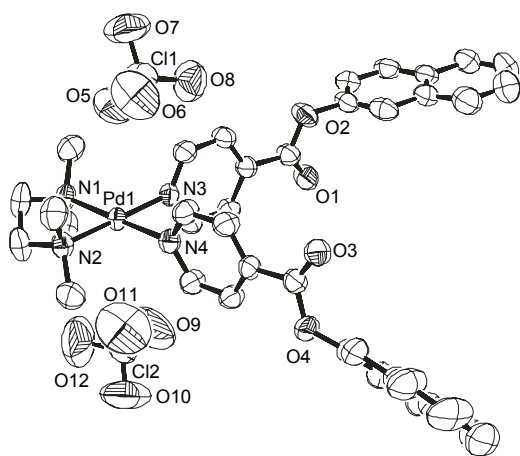
**Table 1.** Crystallographic data for [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·Me<sub>2</sub>CO

	[(Me <sub>4</sub> en)Pd( <i>p</i> -2N) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·Me <sub>2</sub> CO
Formula	C <sub>38</sub> H <sub>38</sub> N <sub>4</sub> O <sub>12</sub> Cl <sub>2</sub> Pd·C <sub>3</sub> H <sub>6</sub> O
<i>M<sub>w</sub></i>	978.10
Space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	16.5545(3)
<i>b</i> , Å	14.5718(3)
<i>c</i> , Å	18.9080(4)
β, deg	100.307(1)
<i>V</i> , Å <sup>3</sup>	4487.6(2)
<i>Z</i>	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>-3</sup>	1.448
μ, mm <sup>-1</sup>	0.599
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0517
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.1257

$${}^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, {}^b wR_2 = \frac{(\sum w(F_o^2 - F_c^2))^2}{\sum wF_o^2}^{1/2}$$

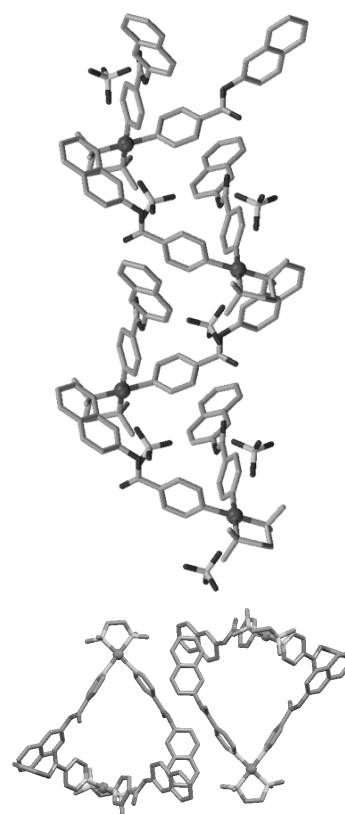
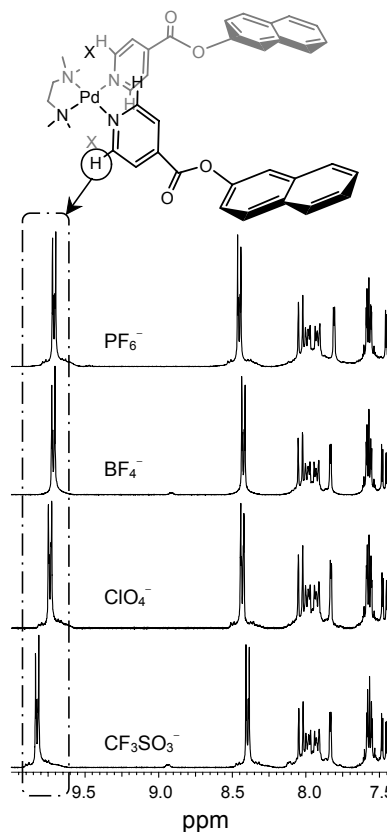
**Table 2.** Selected bond lengths [Å] and angles [°] for [(Me<sub>4</sub>en)Pd(p-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

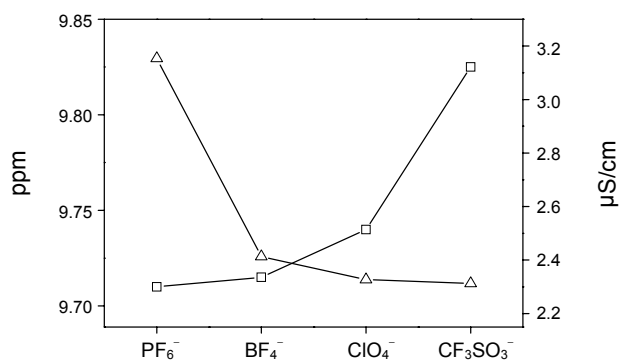
Pd-N(1)	2.336(3)
Pd-N(2)	2.231(3)
Pd-N(3)	2.244(3)
Pd-N(4)	2.336(3)
Pd···O(5)	3.491(4)
Pd···O(11)	3.397(7)
N(1)-Pd-N(2)	86.1(1)
N(3)-Pd-N(4)	85.9(1)
N(1)-Pd-N(4)	179.4(1)
N(2)-Pd-N(3)	179.6(1)

**Figure 1.** ORTEP drawing of [(Me<sub>4</sub>en)Pd(p-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. Hydrogen atoms and solvate molecule were omitted for clarity.

2.244(3) Å, Pd-N(4) = 2.336(3) Å; N(3)-Pd-N(4) = 85.9(1)°). The perchlorate anions are counter ions rather than anionic ligands (Pd···O distances are 3.397(7); 3.491(4) Å). The counter ions were placed at *trans* position of the square plane. Packing diagram shows the packing relationship, even though significant intermolecular interactions do not exist in the solid state (Figure 2). No other exceptional features, neither those of bond lengths nor angles, were observed.

The <sup>1</sup>H NMR spectra of [(Me<sub>4</sub>en)Pd(p-2N)<sub>2</sub>](X)<sub>2</sub> were measured in Me<sub>2</sub>CO-*d*<sub>6</sub> at room temperature (Figure 3). Although all complexes show the similar <sup>1</sup>H NMR patterns, the chemical shifts of 1H-Py are dependent on the counter ions (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> = 9.83 ppm; ClO<sub>4</sub><sup>-</sup> = 9.74 ppm; BF<sub>4</sub><sup>-</sup> = 9.72 ppm; PF<sub>6</sub><sup>-</sup> = 9.71 ppm). BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> complexes are very similar, but CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> complex is significantly deshielded relative to ClO<sub>4</sub><sup>-</sup> complex. For example, the shortest distance between 1H-Py and ClO<sub>4</sub><sup>-</sup> is 2.439 Å. The closer counter ions make the skeletal structure rigid even in solution, resulting in the stronger anisotropy effect. That is, the chemical shifts were deshielded in the order of CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> > ClO<sub>4</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup>. Considering the less metallophilic counter ions, the up field shift of 1H-Py can be explained by the additional fluxional motion of the pyridyl group.<sup>8</sup> Thus, the counter ions significantly affect the pyridyl groups rather than the naphthyl moiety. The naphthyl groups were at remote positions from the palladium(II) cation, and thus were not significantly affected

**Figure 2.** Side view (top) and top view (bottom) of packing structures of [(Me<sub>4</sub>en)Pd(p-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.**Figure 3.** Partial <sup>1</sup>H NMR spectra of [(Me<sub>4</sub>en)Pd(p-2N)<sub>2</sub>](X)<sub>2</sub> (X = PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) in Me<sub>2</sub>CO-*d*<sub>6</sub>.



**Figure 4.** Chemical shift (squares; <sup>1</sup>H-Py) vs conductivity (triangles) of [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](X)<sub>2</sub>.

by the counter ions. Conductivity of the ionic complexes in acetone was measured to confirm the counter ion effects. The conductivity was measured in concentration of 0.25 mM at 25 °C. The conductivity was observed in the order of PF<sub>6</sub><sup>-</sup> (3.15 μS/cm) > BF<sub>4</sub><sup>-</sup> (2.41 μS/cm) > ClO<sub>4</sub><sup>-</sup> (2.33 μS/cm) > CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (2.31 μS/cm) as shown in Figure 4. The order was inversely proportional to the metalophilicity of counter ions. That is, the Hoffmeister series of counter ions<sup>24</sup> may be ordered as CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> > ClO<sub>4</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup> > PF<sub>6</sub><sup>-</sup>. The conductivity of pure acetone as a reference was 0.24 μS/cm at 25 °C.

The present paper reports that the solution-behavior of pyridyl moiety of the palladium(II) complexes is quantitatively dependent on the metalophilicity of counter ions. That is, the <sup>1</sup>H NMR chemical shift of pyridyl group is sensitive to the Hoffmeister series of polyatomic counter ions. These results will contribute to the delicate modulation of facile anion-recognition, in addition to anion sensor, anion transport, and molecular switching.

### Experimental Section

**Materials and measurements.** Most chemicals including potassium tetrachloropalladate(II), *N,N,N',N'*-tetramethylethylenediamine (Me<sub>4</sub>en), and AgX (X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) were purchased from Aldrich, and used without further purification. (Me<sub>4</sub>en)PdCl<sub>2</sub> was prepared according to the procedure described in the literature.<sup>25</sup> <sup>1</sup>H NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz, and the chemical shifts were relative to the internal Me<sub>4</sub>Si. Infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with samples prepared as KBr pellets. Conductivity was measured in acetone using Sartorius Professional Meter PP-50. The melting points were determined with a Thomas-Hoover capillary melting point apparatus and were uncorrected. Elemental microanalyses (C, H, N) were performed on solid samples by the Pusan center, KBSI, using a Vario-EL III.

**Synthesis of 2-naphthalenyl isonicotinate (*p*-2N).** 2-Naphthalenyl isonicotinate was prepared by the literature method.<sup>3</sup> mp 113 - 114 °C. Anal. Calcd. for C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub>: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.12; H, 4.41; N, 5.60. <sup>1</sup>H NMR (300.00 MHz, Me<sub>2</sub>CO-*d*<sub>6</sub>, SiMe<sub>4</sub>): 8.91 (d, *J* = 6.0 Hz, 2H), 8.08 (d, *J* = 6.0 Hz, 2H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.98 (m, 2H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.57 (m, 2H), 7.52 (dd, *J* = 2.1, 9.0 Hz, 1H). <sup>13</sup>C NMR (75 MHz, Me<sub>2</sub>CO-*d*<sub>6</sub>, Me<sub>4</sub>Si): 164.64, 151.82, 149.40,

137.63, 134.70, 132.58, 130.37, 128.67, 128.49, 127.64, 126.84, 123.79, 122.04, 119.51. IR (KBr, cm<sup>-1</sup>): 3360, 1740, 1597, 1508, 1406, 1279, 1153, 823, 750, 480.

**Synthesis of [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.** Silver perchlorate (0.2 mmol, 0.0414 g) in water (5 mL) was added to a suspension of (Me<sub>4</sub>en)PdCl<sub>2</sub> (0.1 mmol, 0.0294 g) in water (5 mL). The reaction mixture was stirred for 2 h at 40 °C, after which precipitated silver chloride was filtered off. To this filtrate was added an acetone (10 mL) solution of *p*-2N (0.2 mmol, 0.0498 g), and the reaction solution was refluxed for 2 h. Then, resulting solution was cooled to room temperature and slowly evaporated in darkness. Single crystals suitable for X-ray single crystallography were formed in a 64% yield. mp 172 - 173 °C (dec.). Anal. Calcd. for C<sub>41</sub>H<sub>44</sub>N<sub>4</sub>O<sub>13</sub>Cl<sub>2</sub>Pd [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·Me<sub>2</sub>CO): C, 49.61; H, 4.16; N, 6.09. Found: C, 49.63; H, 4.12; N, 6.11. <sup>1</sup>H NMR (300.00 MHz, Me<sub>2</sub>CO-*d*<sub>6</sub>, SiMe<sub>4</sub>): 9.74 (d, *J* = 6.6 Hz, 4H), 8.43 (d, *J* = 6.6 Hz, 4H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.96 (m, 4H), 7.83 (d, *J* = 2.1 Hz, 2H), 7.57 (m, 4H), 7.46 (dd, *J* = 2.4, 8.7 Hz, 2H), 2.91 (s, 4H), 2.84 (s, 12H). IR (KBr, cm<sup>-1</sup>): 1757, 1713, 1429, 1284, 1093, 814, 758, 692, 623.

[(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](X)<sub>2</sub> (X<sup>-</sup> = BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) were obtained in the same manner as [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

**[(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>:** mp 165 - 166 °C (dec.). <sup>1</sup>H NMR (300.00 MHz, Me<sub>2</sub>CO-*d*<sub>6</sub>, SiMe<sub>4</sub>): 9.72 (d, *J* = 5.1 Hz, 4H), 8.42 (d, *J* = 5.1 Hz, 4H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.96 (m, 4H), 7.83 (d, *J* = 2.4 Hz, 2H), 7.57 (m, 4H), 7.46 (dd, *J* = 2.7, 9.0 Hz, 2H), 2.88 (s, 12H), 2.83 (s, 4H). IR (KBr, cm<sup>-1</sup>): 1745, 1510, 1466, 1427, 1282, 1061, 812, 756, 692, 476.

**[(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>:** mp 174 - 175 °C (dec.). <sup>1</sup>H NMR (300.00 MHz, Me<sub>2</sub>CO-*d*<sub>6</sub>, SiMe<sub>4</sub>): 9.71 (d, *J* = 5.1 Hz, 4H), 8.45 (d, *J* = 5.1 Hz, 4H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.96 (m, 4H), 7.81 (d, *J* = 2.4 Hz, 2H), 7.57 (m, 4H), 7.44 (dd, *J* = 2.4, 8.7 Hz, 2H), 2.92 (s, 12H), 2.84 (s, 4H). IR (KBr, cm<sup>-1</sup>): 1751, 1425, 1284, 1244, 1159, 841, 758, 557.

**[(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>:** mp 202 - 203 °C (dec.). <sup>1</sup>H NMR (300.00 MHz, Me<sub>2</sub>CO-*d*<sub>6</sub>, SiMe<sub>4</sub>): 9.82 (d, *J* = 5.1 Hz, 4H), 8.40 (d, *J* = 5.1 Hz, 4H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.96 (m, 4H), 7.83 (d, *J* = 2.1 Hz, 2H), 7.57 (m, 4H), 7.47 (dd, *J* = 2.4, 8.7 Hz, 2H), 2.90 (s, 4H), 2.85 (s, 12H). IR (KBr, cm<sup>-1</sup>): 1749, 1431, 1281, 1155, 1028, 812, 756, 638, 517.

**Crystal structure determination.** X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and a CCD detector at 298 K. Thirty six frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the multi-scan method. The structures were solved using the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).<sup>26</sup> The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1.

**Supporting Information.** IR spectra of [(Me<sub>4</sub>en)Pd(*p*-2N)<sub>2</sub>](X)<sub>2</sub> (X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>). X-ray crystallo-

graphic data, in CIF format, for the structure determination of  $[(\text{Me}_4\text{en})\text{Pd}(p\text{-}2\text{N})_2](\text{ClO}_4)_2 \cdot \text{Me}_2\text{CO}$  is deposited with the Cambridge Crystallographic Data Center, CCDC, under supplementary publication number CCDC-790454. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk.

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