Two-Dimensional Double-Metal Cyanide Complexes: Highly Active Catalysts for the Homopolymerization of Propylene Oxide and Copolymerization of Propylene Oxide and Carbon Dioxide

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X-ray analysis of Co(H₂O)₂[Pd(CN)₄] · 4 H₂O

Fig. 1 Top view of the X-ray crystal structure of Co(H₂O)₂[Pd(CN)₄] · 4 H₂O.
Table 1. Crystal data and structure refinement for Co(H$_2$O)$_2$[Pd(CN)$_4$]·4 H$_2$O.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>PdCo</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C$_2$H$_6$Co0.50N2O3Pd0.50</td>
</tr>
<tr>
<td>Formula weight</td>
<td>188.75</td>
</tr>
<tr>
<td>Temperature</td>
<td>105(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.9360 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 12.041(2) Å, α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 14.217(3) Å, β = 90°</td>
</tr>
<tr>
<td></td>
<td>c = 7.4030(15) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1267.3(4) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.979 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>2.745 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>740</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.07 x 0.04 x 0.01 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.09 to 30.09°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>0≤h≤12, 0≤k≤14, 0≤l≤7</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>721</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>721 [R(int) = 0.0000]</td>
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<tr>
<td>Completeness to theta = 22.38°</td>
<td>84.3 %</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>721 / 0 / 79</td>
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<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.144</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0535, wR2 = 0.1599</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0579, wR2 = 0.1651</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.608 and -1.543 e·Å$^{-3}$</td>
</tr>
</tbody>
</table>
Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($\AA^2$ x $10^3$) for Co(H$_2$O)$_2$[Pd(CN)$_4$] $\cdot$ 4 H$_2$O. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
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<td>7500</td>
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<td>Co(1)</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
<td>14(1)</td>
</tr>
<tr>
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<td>7500</td>
<td>4263(7)</td>
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<td>5691(2)</td>
<td>5585(5)</td>
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<td>2500</td>
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<td>8010(7)</td>
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<td>6522(3)</td>
<td>11787(7)</td>
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Table 3. Bond lengths [Å] and angles [°] for Co(H$_2$O)$_2$[Pd(CN)$_4$]·4 H$_2$O.

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<tr>
<th>Bond</th>
<th>Length/Distance</th>
<th>Angle</th>
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<td>Pd(1)-C(1)</td>
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<tr>
<td>Pd(1)-C(1)#1</td>
<td>1.983(5)</td>
<td></td>
</tr>
<tr>
<td>Pd(1)-C(2)#1</td>
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<tr>
<td>Pd(1)-C(2)</td>
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</tr>
<tr>
<td>Co(1)-N(2)</td>
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<tr>
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<tr>
<td>Co(1)-N(1)#2</td>
<td>2.111(4)</td>
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<tr>
<td>Co(1)-N(1)</td>
<td>2.111(4)</td>
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<tr>
<td>N(2)-Co(1)-N(2)#2</td>
<td>91.36(16)</td>
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<td>Co(1)-O(3)#2</td>
<td>2.156(3)</td>
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<td>Co(1)-O(3)</td>
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<tr>
<td>N(1)-C(2)#3</td>
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<td>N(2)-C(1)</td>
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<td>Pd(1)-O(1)</td>
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<td>C(1)-Pd(1)-C(1)#1</td>
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<td>C(1)-Pd(1)-C(2)#1</td>
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<td>C(1)#1-Pd(1)-C(2)#1</td>
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<td>C(1)#1-Pd(1)-C(2)</td>
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</table>

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z  #2 -x+1,-y+1,-z+1  #3 -x+1,-y+1,-z+2
Table 4. Anisotropic displacement parameters (Å\(^2\times 10^3\)) for Co(H\(_2\)O)\(_2\)[Pd(CN)\(_4\)] \cdot 4 H\(_2\)O. The anisotropic displacement factor exponent takes the form: 
\(-2\pi^2 h^2 a^*a^* U^{11} + \ldots + 2hk a^* b^* U^{12}\).

<table>
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<tr>
<th></th>
<th>(U^{11})</th>
<th>(U^{22})</th>
<th>(U^{33})</th>
<th>(U^{23})</th>
<th>(U^{13})</th>
<th>(U^{12})</th>
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<tbody>
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</table>
NMR spectra of poly(PO-co-PC) and PPO

Fig. 2 Full $^1$H NMR spectrum (300 MHz, CDCl$_3$) from Fig. 3A in the text (reference PPC, $f_{CO_2} = 1.0$). See references 5(h) and 22 in the text for polymer synthesis details.

Fig. 3 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of reference PPC used in Fig. 3A of the text ($f_{CO_2} = 1.0$). CCC = Carbonate-Carbonate-Carbonate. See references 5(h) and 22 in the text for polymer synthesis details.
Fig. 4 Full $^1$H NMR spectrum (300 MHz, CDCl$_3$) from Fig. 3B in the text (Table 1, entry 7, $f_{CO_2} = 0.56$).

Fig. 5 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of poly(PO-co-PC) produced in Table 1, entry 7 of the text ($f_{CO_2} = 0.56$). ECC = Ether-Carbonate-Carbonate, ECE = Ether-Carbonate-Ether.
Fig. 6 Full $^1$H NMR spectrum (300 MHz, CDCl$_3$) from Fig. 3C in the text (Table 1, entry 3, $f_{CO_2} = 0.27$).

Fig. 7 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of poly(PO-co-PC) produced in Table 1, entry 3 of the text ($f_{CO_2} = 0.27$).
**Fig. 8** Full $^1$H NMR spectrum (300 MHz, CDCl$_3$) from Fig. 3D in the text (Table 1, entry 14, $f_{CO_2} = 0$).

**Fig. 9** $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of PPO produced in Table 1, entry 14 of the text ($f_{CO_2} = 0$).
Gradient COSY NMR spectrum

Fig. 10 gCOSY spectrum (400 MHz, CDCl$_3$) of poly(PO-co-PC) produced in Table 1, entry 7 of the text ($f_{co_2} = 0.56$).