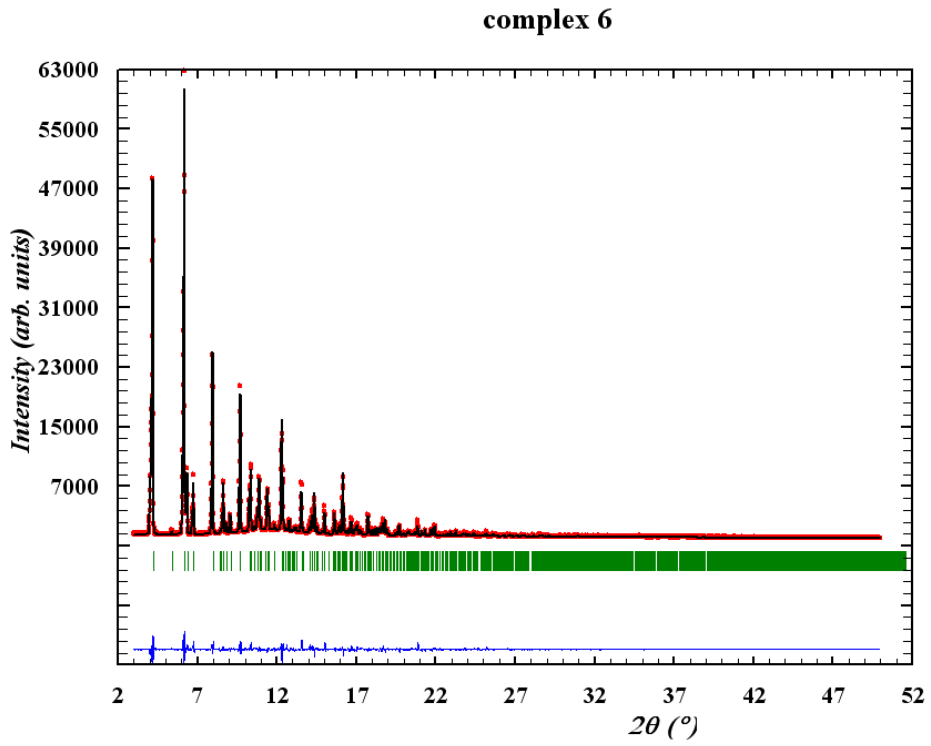
Electronic Supplementary Material (ESI) for CrystEngComm.

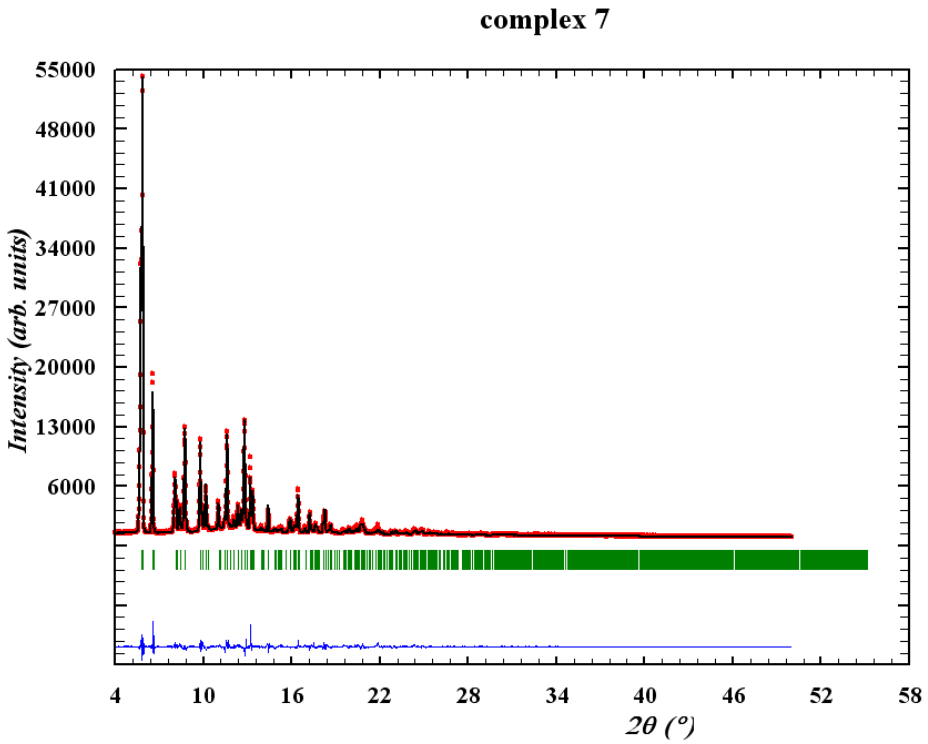

**Table S1. Crystallographic data**

| | **2** | **4** | **5·$(CH_3)_2SO$** | **6** | **7** |
|---|---|---|---|---|---|
| Formula | C22 H16 N6 O6 Pd1 S2 | C18 H20 N2 O6 Pd1 S4 | C18 H22 N2 O8 Pd S4 | C26 H20 N6 O8 Pd1 S2 | C20 H20 N6 O6 Pd1 |
| *M* | 630.92 | 595.00 | 629.02 | 715.01 | 546.82 |
| Crystal system | monoclinic | monoclinic | orthorhombic | monoclinic | monoclinic |
| Space group | P21/c | P21/a | Cmc21 | P21/c | P21/a |
| *Z* | 2 | 2 | 4 | 2 | 2 |
| *a* /Å | 8.0530(3) | 8.3977(14) | 22.245(2) | 12.03223(12) | 9.67234(10) |
| *b* /Å | 9.7220(4) | 11.2186(18) | 13.6954(14) | 14.00604(15) | 14.37138(15) |
| *c* /Å | 16.0510(4) | 12.2070(20) | 7.5899(8) | 9.78155(10) | 8.18547(10) |
| α / º | 90 | 90 | 90 | 90 | 90 |
| β / º | 96.788(2) | 108.288(5) | 90 | 110.8723(13) | 92.73275(10) |
| γ / º | 90 | 90 | 90 | 90 | 90 |
| *V* /Å$^3$ | 1247.84(8) | 1091.9(3) | 2312.3(4) | 1540.25(3) | 1136.53(3) |
| *T* / K | 293(2) | 293(2) | 293(2) | 293(2) | 293(2) |
| λ / Å | 0.71073 | 0.71073 | 0.71073 | 0.82690 | 0.82690 |
| μ / mm$^{-1}$ | 0.962 | 1.271 | 1.212 | | |
| Reflections collected | 10326 | 28341 | 13931 | | |
| Independent reflections | 2890 | 2725 | 2885 | | |
| Goodness-of-fit on $F^2$ | 1.041 | 1.065 | 1.065 | | |
| Final *R* indices [I>2σ(I)][a,b] | 0.0397 | 0.0567 | 0.0396 | | |
| R indices (all data)[a,b] | 0.0772 | 0.0606 | 0.0418 | | |
| Max /min Δ$\rho$[e· Å$^{-3}$] | 0.572<br>-1.229 | 1.609<br>-2.908 | 1.874<br>-0.883 | | |

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ for reflections with I > 2σ I. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all reflections;
$w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, in which $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

**S2. P**lots for the Rietveld refinement of **6** and **7**



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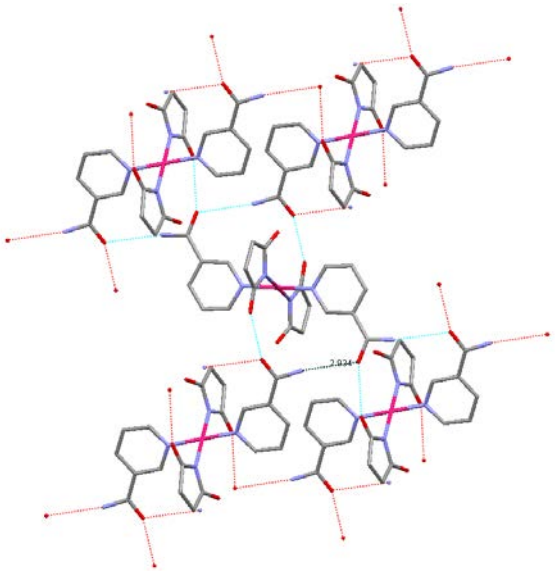
**S3** Crystal packing of $[Pd(succ)_2(nicot)_2]$ (7**)**



**S4.** (B3LYP-D3/def2-TZVPPecp//B3LYP-D3/def2-TZVP) energy diagram (kcal/mol) for rotation of the Pd-S bond in model complex **5**