

**Towards a system for the systematic structural study of  
intermolecular interactions in crystals of transition metal complexes**

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**Supplementary information**

**Table S1** Full list of crystallographic data

|                                                                         | <b>3a</b>                                                                        | <b>3b</b>                                                       | <b>3c</b>                                                         | <b>3d</b>                                                                      | <b>4a</b>                                                        |
|-------------------------------------------------------------------------|----------------------------------------------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------|------------------------------------------------------------------|
| Formula                                                                 | C <sub>36</sub> H <sub>40</sub> Cl <sub>2</sub> CuN <sub>8</sub> O <sub>14</sub> | C <sub>35</sub> H <sub>34</sub> CuN <sub>8</sub> O <sub>5</sub> | C <sub>36</sub> H <sub>36</sub> CuN <sub>8</sub> O <sub>5</sub> S | C <sub>38</sub> H <sub>42</sub> CuN <sub>8</sub> O <sub>6</sub> S <sub>2</sub> | C <sub>40</sub> H <sub>48</sub> CuN <sub>10</sub> O <sub>4</sub> |
| Model Molecular Weight                                                  | 943.20                                                                           | 710.24                                                          | 756.33                                                            | 834.46                                                                         | 860.54                                                           |
| Crystal System                                                          | monoclinic                                                                       | triclinic                                                       | monoclinic                                                        | monoclinic                                                                     | triclinic                                                        |
| Space Group                                                             | <i>P</i> 2 <sub>1</sub> /n(#14)                                                  | <i>P</i> -1(#2)                                                 | <i>P</i> 2 <sub>1</sub> /c(#14)                                   | <i>P</i> 2 <sub>1</sub> /c(#14)                                                | <i>P</i> -1(#2)                                                  |
| <i>a</i>                                                                | 10.982(2) Å                                                                      | 8.6598(3) Å                                                     | 12.366(3) Å                                                       | 15.8052(9) Å                                                                   | 9.992(3) Å                                                       |
| <i>b</i>                                                                | 13.361(3) Å                                                                      | 9.8301(4) Å                                                     | 14.299(3) Å                                                       | 16.1700(10) Å                                                                  | 10.823(3) Å                                                      |
| <i>c</i>                                                                | 14.624(3) Å                                                                      | 10.0256(4) Å                                                    | 19.892(4) Å                                                       | 16.6035(10) Å                                                                  | 11.164(3) Å                                                      |
| $\alpha$                                                                |                                                                                  | 102.016(2)°                                                     |                                                                   |                                                                                | 74.218(4)°                                                       |
| $\beta$                                                                 | 105.488(3)°                                                                      | 98.708(2)°                                                      | 105.054(3)°                                                       | 111.955(3)°                                                                    | 71.368(4)°                                                       |
| $\gamma$                                                                |                                                                                  | 100.635(2)°                                                     |                                                                   |                                                                                | 66.793(4)°                                                       |
| <i>V</i>                                                                | 2068.0(7) Å <sup>3</sup>                                                         | 804.25(5) Å <sup>3</sup>                                        | 3396.6(12) Å <sup>3</sup>                                         | 3935.6(4) Å <sup>3</sup>                                                       | 1036.6(5) Å <sup>3</sup>                                         |
| <i>D</i> <sub>c</sub>                                                   | 1.515 g cm <sup>-3</sup>                                                         | 1.466 g cm <sup>-3</sup>                                        | 1.479 g cm <sup>-3</sup>                                          | 1.408 g cm <sup>-3</sup>                                                       | 1.378 g cm <sup>-3</sup>                                         |
| <i>Z</i>                                                                | 2                                                                                | 1                                                               | 4                                                                 | 4                                                                              | 1                                                                |
| Crystal Size                                                            | 0.350x0.330x0.070 mm                                                             | 1.30x0.40x0.10 mm                                               | 0.263x0.119x0.102 mm                                              | 0.45x0.43x0.15 mm                                                              | 0.278x0.216x0.061 mm                                             |
| Crystal Colour                                                          | blue                                                                             | pale pink                                                       | blue                                                              | pink                                                                           | purple                                                           |
| Crystal Habit                                                           | prism                                                                            | plate                                                           | prism                                                             | plate                                                                          | blade                                                            |
| Temperature                                                             | 150(2) Kelvin                                                                    | 150(2) Kelvin                                                   | 150(2) Kelvin                                                     | 150(2) Kelvin                                                                  | 150(2) Kelvin                                                    |
| $\lambda$ (MoK $\alpha$ )                                               | 0.71073 Å                                                                        | 0.71073 Å                                                       | 0.71073 Å                                                         | 0.71073 Å                                                                      | 0.71073 Å                                                        |
| $\mu$ (MoK $\alpha$ )                                                   | 0.734 mm <sup>-1</sup>                                                           | 0.736 mm <sup>-1</sup>                                          | 0.762 mm <sup>-1</sup>                                            | 0.717 mm <sup>-1</sup>                                                         | 0.681 mm <sup>-1</sup>                                           |
| <i>T</i> (Gaussian) <sub>min,max</sub>                                  | 0.802, 0.921                                                                     | 0.913, 1.000                                                    | 0.818, 0.932                                                      | 0.905, 1.000                                                                   | 0.812, 0.961                                                     |
| 2 $\theta$ <sub>max</sub>                                               | 56.06°                                                                           | 57.58°                                                          | 56.26°                                                            | 58.00°                                                                         | 56.36°                                                           |
| <i>hkl</i> range                                                        | -13 13, -17 17, -18 18                                                           | -11 11, -13 12, -11 13                                          | -15 15, -18 17, -25 25                                            | -21 21, -21 20, -19 22                                                         | -12 13, -13 14, -14 15                                           |
| <i>N</i>                                                                | 18913                                                                            | 7009                                                            | 30324                                                             | 25450                                                                          | 9526                                                             |
| <i>N</i> <sub>ind</sub>                                                 | 4653( <i>R</i> <sub>merge</sub> 0.0286)                                          | 3653( <i>R</i> <sub>merge</sub> 0.0219)                         | 7647( <i>R</i> <sub>merge</sub> 0.0498)                           | 9455( <i>R</i> <sub>merge</sub> 0.0573)                                        | 4521( <i>R</i> <sub>merge</sub> 0.0219)                          |
| <i>N</i> <sub>obs</sub>                                                 | 4230( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                                        | 3129( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                       | 5101( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                         | 6124( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                                      | 3899( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                        |
| <i>N</i> <sub>var</sub>                                                 | 292                                                                              | 232                                                             | 480                                                               | 502                                                                            | 271                                                              |
| Residuals * <i>R</i> 1( <i>F</i> ), <i>R</i> 2( <i>F</i> <sup>2</sup> ) | 0.0278, 0.0758                                                                   | 0.0358, 0.0906                                                  | 0.0379, 0.0795                                                    | 0.0473, 0.1106                                                                 | 0.0355, 0.0877                                                   |
| GoF(all)                                                                | 1.373                                                                            | 1.033                                                           | 1.121                                                             | 1.002                                                                          | 1.200                                                            |
| Residual Extrema e <sup>-</sup> Å <sup>-3</sup>                         | -0.314, 0.408                                                                    | -0.368, 0.523                                                   | -0.372, 0.510                                                     | -0.350, 0.413                                                                  | -0.472, 0.411                                                    |

\*  $R1 = \Sigma ||F_O| - |F_C|| / \Sigma |F_O|$  for  $F_O > 2\sigma(F_O)$ ;  $wR2 = (\Sigma w(F_O^2 - F_C^2)^2 / \Sigma (wF_C^2)^2)^{1/2}$  all reflections

**3a:**  $w=1/[\sigma^2(F_O^2)+(0.03P)^2+0.5P]$  where  $P=(F_O^2+2F_C^2)/3$ ; **3b:**

$w=1/[\sigma^2(F_O^2)+(0.0396P)^2+0.5808P]$  where  $P=(F_O^2+2F_C^2)/3$ ; **3c:**

$w=1/[\sigma^2(F_O^2)+(0.02P)^2+0.5P]$  where  $P=(F_O^2+2F_C^2)/3$ ; **3d:**

$w=1/[\sigma^2(F_O^2)+(0.0453P)^2+0.5136P]$  where  $P=(F_O^2+2F_C^2)/3$ ; **4a:**

$w=1/[\sigma^2(F_O^2)+(0.03P)^2+0.5P]$  where  $P=(F_O^2+2F_C^2)/3$ ; **4b:**

$w=1/[\sigma^2(F_O^2)+(0.02P)^2+1.0P]$  where  $P=(F_O^2+2F_C^2)/3$

**5:**  $w=1/[\sigma^2(F_O^2)+(0.03P)^2+0.2P]$  where  $P=(F_O^2+2F_C^2)/3$

**Table S2** Selected geometry details for **3a** and **3b****3a**

|                 |            |            |            |
|-----------------|------------|------------|------------|
| Cu(1)–N(4)      | 1.9367(13) | Cu(1)–N(1) | 2.0396(12) |
| O(1)–C(1)       | 1.2135(17) | O(2)–C(4)  | 1.3265(17) |
| O(2)–C(5)       | 1.4478(18) | N(1)–C(3)  | 1.3499(18) |
| N(1)–C(1)       | 1.3955(18) | N(2)–C(3)  | 1.3307(18) |
| N(2)–C(2)       | 1.4684(18) | N(3)–C(3)  | 1.3431(18) |
| N(3)–C(4)       | 1.3769(18) | N(4)–C(4)  | 1.2737(19) |
| C(1)–C(2)       | 1.5472(19) |            |            |
|                 |            |            |            |
| N(4)–Cu(1)–N(1) | 88.00(5)   |            |            |

**3b**

|                 |            |            |            |
|-----------------|------------|------------|------------|
| Cu(1)–N(4)      | 1.9251(16) | Cu(1)–N(1) | 2.0322(16) |
| O(1)–C(1)       | 1.225(2)   | O(2)–C(4)  | 1.352(2)   |
| O(2)–C(5)       | 1.435(2)   | N(1)–C(1)  | 1.373(2)   |
| N(1)–C(3)       | 1.377(2)   | N(2)–C(3)  | 1.341(2)   |
| N(2)–C(2)       | 1.455(2)   | N(3)–C(3)  | 1.324(2)   |
| N(3)–C(4)       | 1.350(2)   | N(4)–C(4)  | 1.287(3)   |
| C(1)–C(2)       | 1.550(3)   |            |            |
|                 |            |            |            |
| N(4)–Cu(1)–N(1) | 87.67(7)   |            |            |

**Table S3** Selected geometry details for **3c** and **3d****3c**

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| Cu(1)–N(4)      | 1.931(2)   | Cu(1)–N(8)      | 1.936(2)   |
| Cu(1)–N(1)      | 2.0468(17) | Cu(1)–N(5)–     | 2.0495(18) |
| Cu(1)–O(5)      | 2.4013(17) | O(1)–C(1)       | 1.228(2)   |
| O(2)–C(4)       | 1.349(3)   | O(2)–C(5)       | 1.432(3)   |
| O(3)–C(18)      | 1.226(3)   | O(4)–C(21)      | 1.354(3)   |
| O(4)–C(22)      | 1.434(3)   | N(1)–C(1)       | 1.362(3)   |
| N(1)–C(3)       | 1.385(3)   | N(2)–C(3)       | 1.341(3)   |
| N(2)–C(2)       | 1.440(3)   | N(3)–C(3)       | 1.319(3)   |
| N(3)–C(4)       | 1.355(3)   | N(4)–C(4)       | 1.279(3)   |
| N(5)–C(18)      | 1.367(3)   | N(5)–C(20)      | 1.378(3)   |
| N(6)–C(20)      | 1.338(3)   | N(6)–C(19)      | 1.449(3)   |
| N(7)–C(20)      | 1.321(3)   | N(7)–C(21)      | 1.355(3)   |
| N(8)–C(21)      | 1.284(3)   | C(1)–C(2)       | 1.554(3)   |
|                 |            |                 |            |
| N(4)–Cu(1)–N(8) | 171.74(8)  | N(4)–Cu(1)–N(1) | 87.12(8)   |
| N(8)–Cu(1)–N(1) | 93.16(8)   | N(4)–Cu(1)–N(5) | 91.85(8)   |
| N(8)–Cu(1)–N(5) | 87.41(8)   | N(1)–Cu(1)–N(5) | 176.69(7)  |

**3d**

|                 |            |                 |           |
|-----------------|------------|-----------------|-----------|
| Cu(1)–N(4)      | 1.897(2)   | Cu(1)–N(8)      | 1.908(2)  |
| Cu(1)–N(5)      | 2.033(2)   | Cu(1)–N(1)      | 2.034(2)  |
| O(1)–C(1)       | 1.222(3)   | O(2)–C(4)       | 1.349(3)  |
| O(2)–C(5)       | 1.436(3)   | O(3)–C(18)      | 1.223(3)  |
| O(4)–C(21)      | 1.352(3)   | O(4)–C(22)      | 1.434(3)  |
| N(1)–C(3)       | 1.382(3)   | N(1)–C(1)       | 1.382(3)  |
| N(2)–C(3)       | 1.335(3)   | N(2)–C(2)       | 1.450(3)  |
| N(3)–C(3)       | 1.327(3)   | N(3)–C(4)       | 1.335(3)  |
| N(4)–C(4)       | 1.300(3)   | N(5)–C(18)      | 1.379(3)  |
| N(5)–C(20)      | 1.379(3)   | N(6)–C(20)      | 1.343(3)  |
| N(6)–C(19)      | 1.452(3)   | N(7)–C(20)      | 1.325(3)  |
| N(7)–C(21)      | 1.344(3)   | N(8)–C(21)      | 1.287(3)  |
| C(1)–C(2)       | 1.545(3)   |                 |           |
|                 |            |                 |           |
| N(4)–Cu(1)–N(8) | 175.74(10) | N(4)–Cu(1)–N(5) | 92.15(8)  |
| N(8)–Cu(1)–N(5) | 87.71(8)   | N(4)–Cu(1)–N(1) | 87.24(9)  |
| N(8)–Cu(1)–N(1) | 93.32(9)   | N(5)–Cu(1)–N(1) | 174.28(8) |

**Table S4** Selected geometry details for **4a** and **4b**

**4a**

|                 |            |            |            |
|-----------------|------------|------------|------------|
| Cu(1)–N(4)      | 1.9041(17) | Cu(1)–N(1) | 2.0458(15) |
| O(1)–C(1)       | 1.227(2)   | N(1)–C(1)  | 1.366(2)   |
| N(1)–C(3)       | 1.393(2)   | N(2)–C(3)  | 1.350(2)   |
| N(2)–C(2)       | 1.447(2)   | N(3)–C(3)  | 1.307(2)   |
| N(3)–C(4)       | 1.366(2)   | N(4)–C(4)  | 1.312(2)   |
| N(5)–C(4)       | 1.358(2)   | N(5)–C(6)  | 1.454(2)   |
| N(5)–C(5)       | 1.459(3)   | C(1)–C(2)  | 1.550(3)   |
|                 |            |            |            |
| N(4)–Cu(1)–N(1) | 87.53(7)   |            |            |

**4b**

|                 |            |            |            |
|-----------------|------------|------------|------------|
| Ni(1)–N(4)      | 1.8679(19) | Ni(1)–N(1) | 1.9652(18) |
| O(1)–C(1)       | 1.224(3)   | N(1)–C(1)  | 1.367(3)   |
| N(1)–C(3)       | 1.396(3)   | N(2)–C(3)  | 1.343(3)   |
| N(2)–C(2)       | 1.438(3)   | N(3)–C(3)  | 1.298(3)   |
| N(3)–C(4)       | 1.359(3)   | N(4)–C(4)  | 1.307(3)   |
| N(5)–C(4)       | 1.360(3)   | N(5)–C(6)  | 1.450(3)   |
| N(5)–C(5)       | 1.452(3)   | C(1)–C(2)  | 1.545(3)   |
|                 |            |            |            |
| N(4)–Ni(1)–N(1) | 88.12(8)   |            |            |