Cocrystallization of Energetic Mn(II) Complex with Nitrogen-rich Ligand SCZ and Oxygen-rich Ligand TNR

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Supporting Information Placeholder

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| items                          | structure parameters                        |
|-------------------------------|---------------------------------------------|
| CCDC No.                      | 1010969                                     |
| Empirical formula             | \(\text{C}_{17}\text{H}_{33}\text{Mn}_2\text{N}_2\text{O}_{24}\) |
| Formula weight                | 1025.52                                     |
| T/K                           | 153(2)                                      |
| Crystal system                | Triclinic                                   |
| Space group                   | P-1                                         |
| a, b, c /Å                    | 10.1738(17), 12.428(2), 15.043(2)           |
| \(\alpha, \beta, \gamma/°\) | 79.184(6), 80.480(5), 80.735(5)             |
| \(V/Å^3\)                     | 1825.9(5)                                   |
| Z                             | 2                                           |
| Calculated density/(g·cm\(^{-3}\)) | 1.8651                                     |
| \(\theta\) range / (°)       | 2.05~31.53                                  |
| h, k, l                       | -14~14, -17~18, -21~22                     |
| Measured reflections          | 11947                                       |
| Rint                          | 0.0308                                      |
| S                             | 1.0018                                      |
| \(R_1, wR_2[I>2\sigma(I)]\)  | 0.0449, 0.1039                              |
| \(R_1, wR_2(\text{all data})\) | 0.0453, 0.1115                             |
| \(\mu(\text{MoK}\alpha)/\text{mm}^{-1}\) | 0.816                                       |
| \(F\)                         | 1048                                        |

\[a\] \(w=1/\sigma^2(\text{Fo})^2+(0.0.0683p)^2+3.9930p\]. \(p=(\text{Fo}^2+2\text{Fc}^2)/3\)

Table S2 Crystallographic data and structure parameters for \([\text{Mn(SCZ)}_2(\text{H}_2\text{O})(\text{TNR})]\cdot3(\text{H}_2\text{O})\)

| items                          | structure parameters                        |
|-------------------------------|---------------------------------------------|
| CCDC No.                      | 1865398                                     |
| Empirical formula             | \(\text{C}_8\text{H}_{19}\text{MnN}_9\text{O}_{14}\) |
| Formula weight                | 520.26                                      |
| T/K                           | 153(2)                                      |
| Crystal system                | Monoclinic                                  |
| Space group                   | P21/c                                       |
| a, b, c /Å                    | 11.226(2), 6.7846(14), 25.580(5)            |
| \(\alpha, \beta, \gamma/°\) | 90, 98.07(3), 90                           |
| \(V/Å^3\)                     | 199.0(7)                                    |
| Z                             | 4                                           |
| Calculated density/(g·cm\(^{-3}\)) | 1.791                                      |
| \(\theta\) range / (°)       | 2.6~27.5                                    |
| h, k, l                       | -14~14, -8~8, -33~33                       |
| Rint                          | 0.046                                       |
| S                             | 1.0018                                      |
| \(R_1, wR_2\)                 | 0.0449, 0.1039                              |
| \(\mu(\text{MoK}\alpha)/\text{mm}^{-1}\) | 0.779                                       |
| \(F\)                         | 1068                                        |

Table S3 Selected bond lengths and bond angles for \([\text{Mn(SCZ)}_3(\text{TNR})(\text{H}_2\text{O})]\cdot[\text{Mn(SCZ)}_2(\text{H}_2\text{O})(\text{TNR})](\text{H}_2\text{O})\)

| Bond Angles / ° | Bond Distances / Å |
|----------------|--------------------|
| O1-Mn1-O3      | 80.02(5)           |
| O1-Mn1-N1      | 71.60(5)           |
| O1-Mn1-N4      | 78.33(5)           |
| O1-Mn1-N7      | 131.77(5)          |
| O2-Mn1-O3      | 86.67(5)           |
| O2-Mn1-O6      | 75.74(5)           |
| O2-Mn1-N4      | 71.38(5)           |
| O2-Mn1-N7      | 87.46(5)           |
| Bond Angles / ° | Bond Distances / Å |
|----------------|--------------------|
| O3-Mn1-N1 | 117.10(5) | Mn2-O15 | 2.0120(15) |
| O3-Mn1-N4 | 125.88(5) | Mn2-N13 | 2.2754(15) |
| O3-Mn1-N7 | 72.48(5) | Mn2-N16 | 2.2983(16) |
| O6-Mn1-N1 | 76.55(5) | Mn2-O12 | 2.1851(13) |
| O6-Mn1-N4 | 73.45(5) | O1-C1 | 1.262(2) |
| O6-Mn1-N7 | 80.33(5) | O2-C2 | 1.257(2) |
| N1-Mn1-N4 | 101.83(6) | O3-C3 | 1.259(2) |
| N1-Mn1-N7 | 86.62(5) | O4-C4 | 1.262(2) |
| O12-Mn2-N13 | 73.52(5) | O5-N10 | 1.236(2) |
| O12-Mn2-N16 | 87.67(5) | O6-N10 | 1.248(2) |
| O13-Mn2-O14 | 87.80(5) | O7-N11 | 1.232(2) |
| O13-Mn2-O15 | 106.07(6) | O8-N11 | 1.237(2) |
| O13-Mn2-N16 | 73.16(5) | O9-C8 | 1.270(2) |

Table S4: Selected hydrogen bonds for [Mn(SCZ)$_3$]($\text{TNR}$)($\text{H}_2\text{O}$)$\cdot$[Mn(SCZ)$_2$($\text{H}_2\text{O}$)($\text{TNR}$)]($\text{H}_2\text{O}$)

| D-H...A | D...A / Å | D-H/A° |
|---------|-----------|--------|
| N1-H1A...O8 | N1-H1A...O9 | 3.023(2) | 143.00 |
| N1-H1B...O5 | N1-H1B...O8 | 2.910(2) | 105.00 |
| N2--H2...O4 | N2--H2...O5 | 2.756(2) | 152.00 |
| N3--H3A...O4 | N3--H3B...O1 | 2.834(2) | 150.00 |
| N4--H4A...O9 | N4--H4B...O11 | 3.125(2) | 158.00 |
| N5--H5...O24 | N5--H5...O11 | 2.984(3) | 144.00 |
| N6--H6A...O24 | N6--H6B...O23 | 2.923(3) | 147.00 |
| N7--H7A...O8 | N7--H7A...O18 | 3.367(2) | 166.00 |
| N7--H7B...O17 | N8--H8...O18 | 2.751(2) | 130.00 |
| N8--H8...O21 | N8--H8...O21 | 3.156(2) | 141.00 |
| N9--H9A...O21 | N9--H9B...O12 | 2.991(2) | 157.00 |
| N9--H9B...O12 | N10--H10A...O16 | 2.915(2) | 168.00 |
| N13--H13A...O19 | N13--H13A...O19 | 2.892(2) | 112.00 |
| N13--H13A...O19 | N13--H13B...O4 | 2.994(2) | 131.00 |
| O14--H14A...O3 | O14--H14A...O3 | 2.918(2) | 164.00 |
| O14--H14B...O10 | O14--H14B...O10 | 3.002(2) | 147.00 |
| O15--H15B...O9 | O15--H15B...O9 | 7624(19) | 176.00 |
| O15--H15B...O9 | O15--H15B...O10 | 2.889(2) | 153.00 |
| O16--H16B...O19 | O16--H16B...O19 | 2.878(2) | 122.00 |
| O16--H16B...O20 | O16--H16B...O20 | 2.738(2) | 124.00 |
Symmetry codes: a = x,1+y,z; b = 1+x,y,z; c = 2

Table S5 Selected bond lengths and bond angles for [Mn(SCZ₂)(H₂O)(TNR)]·3(H₂O)

| Bond Angles / ° | Bond Distances/ Å |
|-----------------|-------------------|
| O8-Mn1-O9      | 101.08(6)         | Mn1-O8          | 12.49(16) |
| O8-Mn1-O10     | 113.80(7)         | Mn1-O9          | 12.16(16) |
| O8-Mn1-O11     | 150.34(7)         | Mn1-O10         | 12.34(17) |
| O8-Mn1-N5      | 96.13(7)          | Mn1-O11         | 212.20(17) |
| O8-Mn1-N7      | 78.48(7)          | Mn1-N5          | 23.39(2)  |
| O9-Mn1-O10     | 79.96(7)          | Mn1-N7          | 22.63(2)  |
| O9-Mn1-O11     | 89.35(7)          | O1-N1           | 12.37(3)  |
| O9-Mn1-N5      | 151.73(7)         | O2-N1           | 12.22(3)  |
| O9-Mn1-N7      | 102.77(8)         | O3-N2           | 12.41(3)  |
| O10-Mn1-O11    | 95.25(7)          | O4-N2           | 12.33(3)  |
| O10-Mn1-N5     | 72.60(7)          | O5-N3           | 12.43(3)  |
| O10-Mn1-N7     | 166.91(8)         | O6-N3           | 12.35(3)  |
| O11-Mn1-N5     | 86.57(7)          | O7-C21          | 12.60(3)  |
| O11-Mn1-N7     | 72.12(7)          | O8-C30          | 12.75(3)  |
| N5-Mn1-N7      | 102.53(8)         | O10-C31         | 12.54(2)  |
| Mn1-O8-C30     | 139.89(14)        | O11-C22         | 12.56(3)  |
| Mn1-O10-C31    | 118.00(15)        | N2-C8           | 12.44(3)  |
| Mn1-O11-C22    | 116.37(14)        | N3-C28          | 12.48(3)  |
| H9A-O9-H9B     | 103.00            | N4-N5           | 12.14(3)  |
| Mn1-O9-H9A     | 105.00            | N4-C31          | 12.35(3)  |
| Mn1-O9-H9B     | 121.00            | N6-N7           | 12.08(3)  |
| O3-N2-C8       | 119.7(2)          | N6-C22          | 12.34(3)  |
| O4-N2-C8       | 119.0(2)          | N8-C22          | 12.40(3)  |
| O6-N3-C28      | 119.75(19)        | N9-C31          | 12.34(3)  |
| O5-N3-O6       | 121.2(2)          | O9-H9A          | 0.8400    |
| O5-N3-C28      | 119.0(2)          | N4-H4           | 0.8500    |
| N5-N4-C31      | 116.85(19)        | C8-C21          | 1.445(3)  |
| Mn1-N5-N4      | 106.48(13)        | C8-C20          | 1.381(3)  |

Table S6 Selected hydrogen bonds for [Mn(SCZ₂)(H₂O)(TNR)]·3(H₂O)

| D-H...A     | D...A / Å | D-H/Å° |
|-------------|-----------|--------|
| N4--H4...O1 | 3.028(3)  | 146.00 |
| N4--H4...O8 | 3.133(3)  | 141.00 |
| N5--H5A...O6| 3.070(3)  | 137.00 |
| N5--H5B...O3| 3.116(3)  | 172.00 |
| N6--H6...O3 | 3.101(3)  | 134.00 |
| N6--H6...O7 | 2.690(3)  | 150.00 |
| N7--H7A...O5| 3.025(3)  | 160.00 |
| N7--H7B...O6| 2.896(3)  | 130.00 |
| N8--H8A...O2| 3.067(3)  | 138.00 |
| D-H..A           | D...A / Å    | D–H/Å°  |
|-----------------|-------------|---------|
| N8–H8A...O7     | 2.900(3)    | 140.00  |
| N8–H8B...O12    | 3.007(3)    | 141.00  |
| O9–H9A...O14    | 2.842(2)    | 173.00  |
| O9–H9B...O14    | 2.720(2)    | 173.00  |
| N9–H9C...O1     | 3.017(3)    | 137.00  |
| N9–H9D...O13    | 2.956(3)    | 164.00  |
| O12–H12A...O1   | 2.882(3)    | 141.00  |
| O12–H12A...O10  | 3.181(3)    | 137.00  |
| O12–H12B...N9   | 3.294(3)    | 165.00  |
| O13–H13A...O12  | 2.722(3)    | 164.00  |
| O13–H13B...O7   | 2.766(3)    | 176.00  |
| O14–H14A...O13  | 2.768(3)    | 155.00  |
| O14–H14B...O11  | 2.765(2)    | 176.00  |
| C20–H20...O4    | 2.683(3)    | 100.00  |

Symmetry codes: a = x,1+y,z; b = -1+x,y,z; c = -x,-1/2+y,1/2-z; d = -x,y,1-z; e = -x,2-y,1-z; f = 1-x,1-y,1-z; g = 1-x,2-y,1-z; h = -1+x,y,z; j = x,3/2-y,-1/2+z; l = x,-1+y,z; m = 1+x,y,z; n = 1-x,-1/2+y,1/2-z; r = -x,1/2+y,1/2-z; s = 1-x,1/2+y,1/2-z; t = -1-x,1/2+y,1/2-z; v = x,3/2-y,1/2+z.

Figure S1 The fully labeled molecular structure of [Mn(SCZ)3](TNR)(H2O) (component A)

Figure S2 The fully labeled molecular structure of [Mn(SCZ)2(H2O)(TNR)](H2O) (component B)
Figure S3 The fully labeled molecular structure of [Mn(SCZ)₃](TNR)(H₂O)·[Mn(SCZ)₂(H₂O)(TNR)](H₂O) (cocrystal)

Figure S4 The fully labeled molecular structure of [Mn(SCZ)₂(H₂O)(TNR)]·3(H₂O)

Figure S5 The fully labeled molecular structure of [Mn(SCZ)₃](PA)₂(H₂O) [1]
Sensitivity test

The impact sensitivity of the cocrystal \([\text{Mn(SCZ)}_3](\text{TNR})(\text{H}_2\text{O}))\cdot[\text{Mn(SCZ)}_2(\text{H}_2\text{O})(\text{TNR})](\text{H}_2\text{O})\) and \([\text{Mn(SCZ)}_2(\text{H}_2\text{O})(\text{TNR})](\text{H}_2\text{O})\) was tested by Fall Hammer Method using a 5 kg drop hammer. The result shows that the firing rate was 0% for these two complexes at 80 cm height. Friction sensitivity was determined by using 20 mg sample on a Julius Peter’s machine and both of the compounds did not fire. The results indicate that the cocrystal and \([\text{Mn(SCZ)}_2(\text{H}_2\text{O})(\text{TNR})](\text{H}_2\text{O})\) are insensitive.

References

[6] G. X. Ma, T. L. Zhang, B. Shao, J. G. Zhang, J. C. Song, Y. F. Li, K. B. Yu. *Chinese J. Struct. Chem.*, *23*, 451 (2004).