Supplementary Materials

A series of field-induced single-ion magnets based on the seven-coordinate Co(II) complexes with the pentadentate (*N3O2*) H2dapsc ligand

Vyacheslav A. Kopotkov 1,\*, Denis V. Korchagin 1,\*, Valentina D. Sasnovskaya 1, Ildar F. Gilmutdinov 2 and Eduard B. Yagubskii 1,\*

1 Institute of Problems of Chemical Physics, Russian Academy of Sciences, Semenov’s av., 1, Chernogolovka 142432, Moscow Region, Russia; slavaoven@mail.ru (V.A.K.); korden@icp.ac.ru (D.V.K); sasnovskayavd@rambler.ru (V.D.S); yagubski@icp.ac.ru (E.B.Y.);

2 Institute of Physics, Kazan Federal University, 16a Kremlyovskaya st., Kazan, Republic of Tatarstan, Russia; [ildar.gilmutdinov@gmail.com](https://e.mail.ru/compose/?mailto=mailto%3aildar.gilmutdinov@gmail.com) (I.F.G.);

**\*** Correspondence: slavaoven@mail.ru (V.A.K.); korden@icp.ac.ru (D.V.K); yagubski@icp.ac.ru (E.B.Y.) +74965221256 (V.A.K.); +74965221531 (D.V.K.); +74965221185

**Table S1.** Shape analysis for the metal centers of complexes **1-7**.

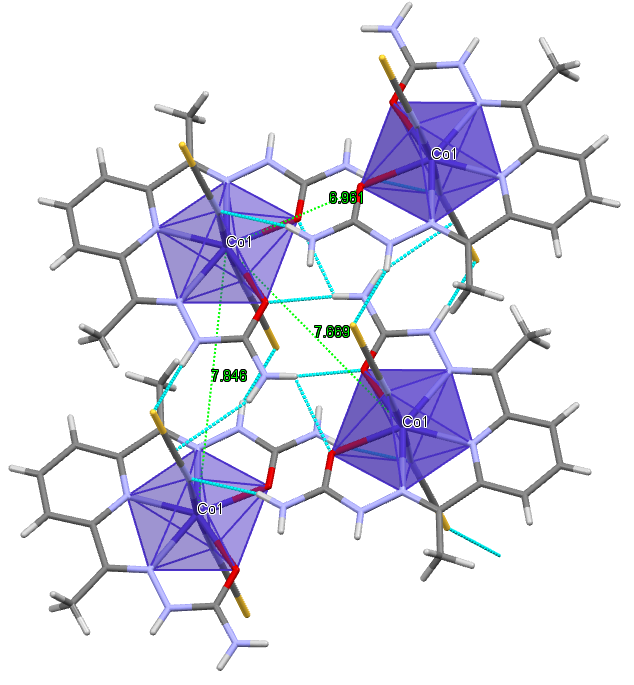
|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Structure [ML7 ] | HP-7 | HPY-7 | PBPY-7 | COC-7 | CTPR-7 | JPBPY-7 | JETPY-7 |
| **1** | 32.702 | 22.860 | 0.312 | 7.091 | 5.497 | 3.075 | 23.180 |
| **2** | 32.546 | 22.903 | 0.314 | 7.133 | 5.528 | 3.028 | 23.191 |
| **3** | 34.400 | 25.544 | 0.058 | 7.964 | 6.188 | 3.746 | 24.317 |
| **4** | 33.326 | 23.153 | 0.294 | 7.266 | 5.377 | 3.302 | 22.421 |
| **5a** | 34.305 | 24.619 | 0.105 | 7.480 | 5.670 | 3.583 | 23.866 |
| **5b** | 33.901 | 25.280 | 0.072 | 7.895 | 6.032 | 3.641 | 24.031 |
| **6** | 33.964 | 23.539 | 0.191 | 7.563 | 6.013 | 3.460 | 23.328 |
| **7** | 33.417 | 23.949 | 0.499 | 7.592 | 5.710 | 5.024 | 22.597 |

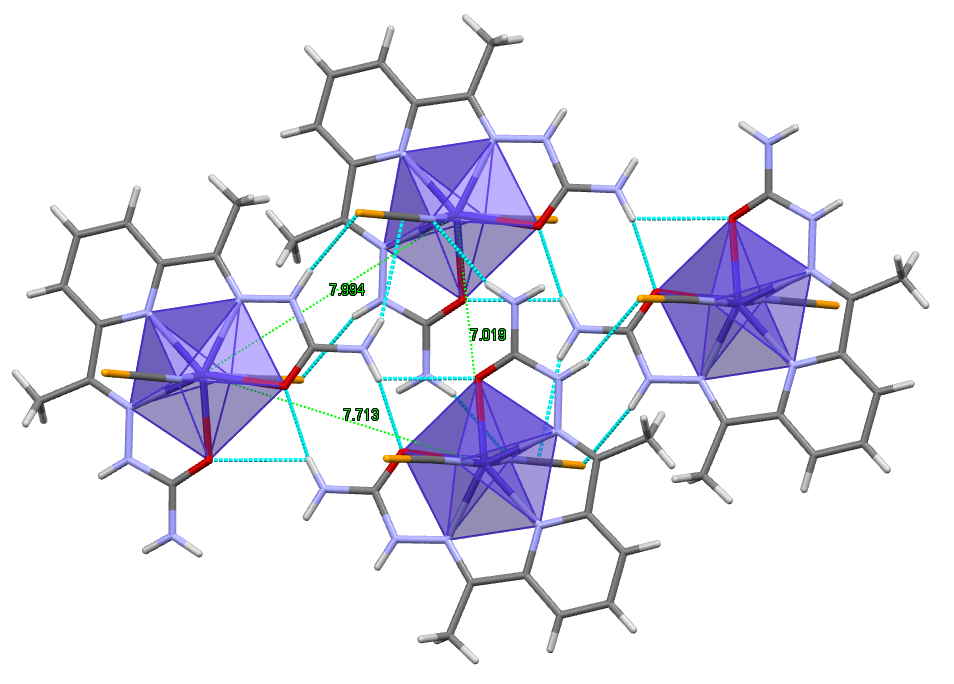
**HP-7** Heptagon (*D7h*) , **HPY-7** Hexagonal pyramid (*C6v*), **PBPY-7** Pentagonal bipyramid (*D5h*), **COC-7** Capped octahedron\* (*C3v*), **CTPR-7** Capped trigonal prism \* (*C2v*), **JPBPY-7** Johnson pentagonal bipyramid (J13) (*D5h*), **JETPY-7** Elongated triangular pyramid (J7) (*C3v*)

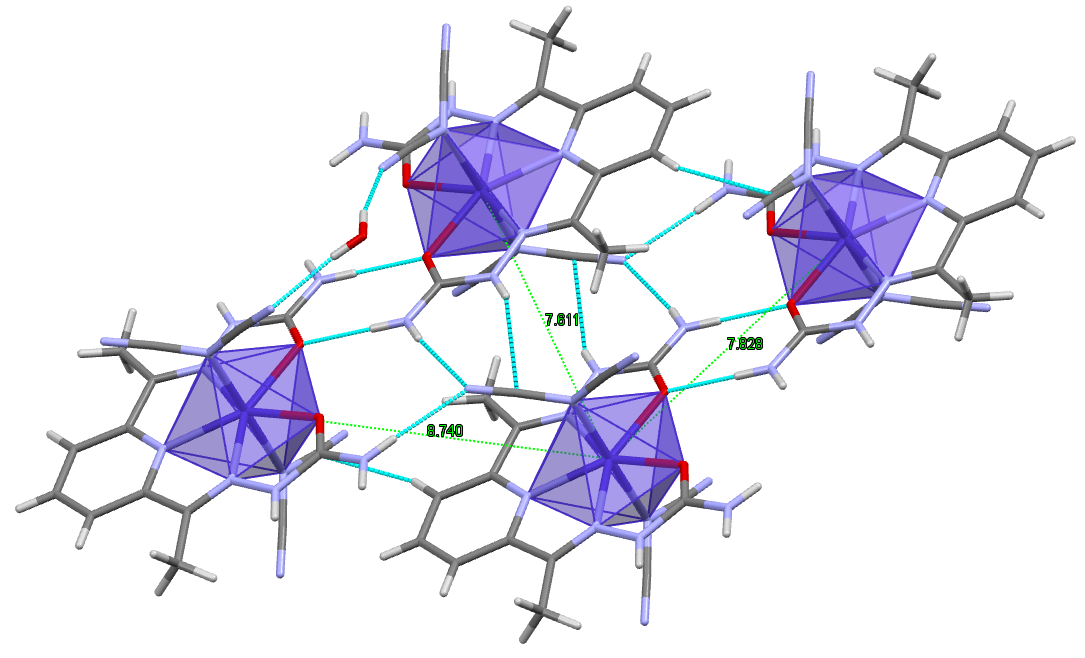
**Table S2**. Selected bond lengths (Å) and angles (°) in coordination polyhedraof **1**-**7**

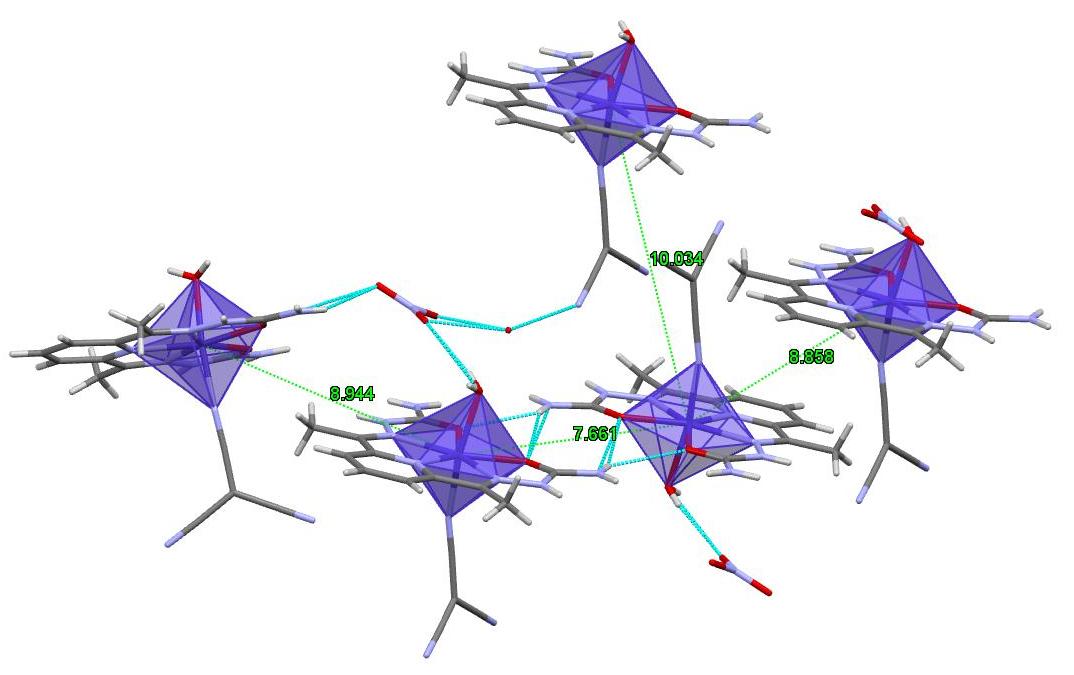
|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
| ***Bond*** |  |  |  |  |  |  |  |
| Co(1)-N(1){X*a*} | 2.080(2) | 2.079(3) | 2.181(2) | 2.104(2) | 2.195(2) | 2.119(2) | 2.476(2) |
| Co(1)-N(2){O(3)} | 2.124(2) | 2.114(3) | 2.194(2) | 2.135(2) | 2.161(2) | 2.182(2) | 2.137(6) |
| Co(1)-N(3) | 2.225(2) | 2.223(2) | 2.189(2) | 2.202(2) | 2.202(2) | 2.204(2) | 2.196(7) |
| Co(1)-N(4) | 2.184(2) | 2.185(2) | 2.170(2) | 2.195(2) | 2.182(2) | 2.192(2) | 2.189(5) |
| Co(1)-N(5) | 2.186(2) | 2.185(2) | 2.203(2) | 2.195(2) | 2.196(2) | 2.206(2) | 2.186(7) |
| Co(1)-O(1) | 2.218(1) | 2.224(2) | 2.156(1) | 2.190(2) | 2.161(2) | 2.206(2) | 2.165(6) |
| Co(1)-O(2) | 2.230(1) | 2.230(2) | 2.171(2) | 2.179(2) | 2.189(2) | 2.159(2) | 2.186(6) |
| ***Angle*** |  |  |  |  |  |  |  |
| {X}N(1)-Co(1)-N(2){O(3)} | 174.01(7) | 174.3(1) | 177.32(7) | 171.21(9) | 178.51(9) | 173.96(9) | 176.2(2) |
| {X}N(1)-Co(1)-N(4) | 95.56(6) | 95.71(9) | 90.73(7) | 94.48(8) | 90.15(8) | 92.61(7) | 90.0(2) |
| {O(3)}N(2)-Co(1)-N(4) | 90.17(6) | 89.70(9) | 89.62(7) | 92.80(9) | 90.82(8) | 93.40(7) | 92.8(2) |
| {X}N(1)-Co(1)-N(5) | 90.65(6) | 90.66(9) | 92.23(7) | 92.07(9) | 89.57(8) | 90.98(8) | 95.3(2) |
| {O(3)}N(2)-Co(1)-N(5) | 89.64(6) | 89.45(9) | 90.39(7) | 85.75(10) | 89.68(8) | 91.48(7) | 86.9(2) |
| N(4)-Co(1)-N(5) | 70.50(6) | 70.57(8) | 70.23(7) | 70.29(9) | 70.46(9) | 70.02(8) | 70.4(3) |
| {X}N(1)-Co(1)-O(1) | 84.35(6) | 84.09(9) | 89.07(6) | 90.66(9) | 89.00(8) | 88.16(6) | 83.6(2) |
| {O(3)}N(2)-Co(1)-O(1) | 92.33(6) | 92.88(9) | 89.05(6) | 86.69(9) | 90.95(8) | 86.89(7) | 92.8(2) |
| N(4)-Co(1)-O(1) | 140.45(5) | 140.58(8) | 143.09(6) | 141.52(8) | 141.63(8) | 141.27(7) | 141.8(3) |
| N(5)-Co(1)-O(1) | 148.93(6) | 148.71(8) | 146.66(7) | 147.67(7) | 147.88(8) | 148.71(8) | 146.8(3) |
| {X}N(1)-Co(1)-N(3) | 90.06(6) | 90.18(9) | 88.30(7) | 91.52(9) | 92.53(8) | 90.54(6) | 85.8(2) |
| {O(3)}N(2)-Co(1)-N(3) | 93.54(6) | 93.37(9) | 89.31(7) | 95.59(9) | 88.86(8) | 91.10(7) | 94.5(3) |
| N(4)-Co(1)-N(3) | 69.84(6) | 69.87(8) | 70.83(6) | 70.11(9) | 70.18(9) | 70.22(8) | 70.3(3) |
| N(5)-Co(1)-N(3) | 140.22(6) | 140.31(8) | 141.06(7) | 140.40(9) | 140.58(8) | 140.24(6) | 140.7(3) |
| O(1)-Co(1)-N(3) | 70.61(5) | 70.72(7) | 72.27(6) | 71.65(8) | 71.54(8) | 71.05(7) | 71.9(3) |
| {X}N(1)-Co(1)-O(2) | 88.38(6) | 88.39(9) | 90.19(6) | 87.39(8) | 88.34(8) | 88.63(7) | 90.4(2) |
| {O(3)}N(2)-Co(1)-O(2) | 86.05(6) | 86.25(9) | 91.19(6) | 83.84(8) | 90.20(8) | 86.95(7) | 87.3(2) |
| N(4)-Co(1)-O(2) | 141.71(5) | 141.79(8) | 141.34(6) | 142.02(9) | 142.23(8) | 141.26(7) | 141.7(3) |
| N(5)-Co(1)-O(2) | 71.38(5) | 71.41(8) | 71.12(6) | 71.73(7) | 71.80(8) | 71.25(7) | 71.4(2) |
| O(1)-Co(1)-O(2) | 77.82(5) | 77.60(7) | 75.56(6) | 76.23(7) | 76.08(7) | 77.46(6) | 76.4(2) |
| N(3)-Co(1)-O(2) | 148.39(5) | 148.27(8) | 147.81(6) | 147.85(9) | 147.88(8) | 148.51(8) | 147.8(3) |

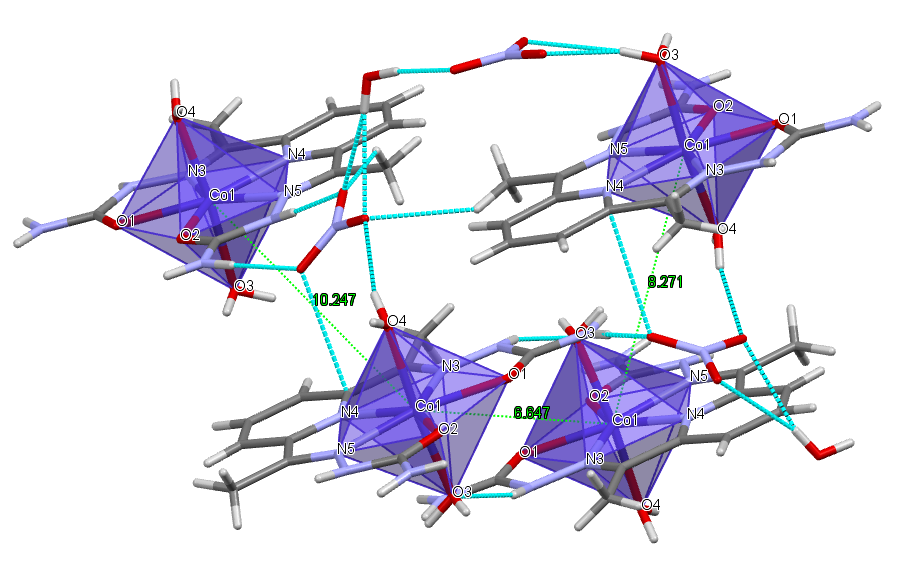
*a* X = O(4),Cl(1) in compounds **6** and **7**

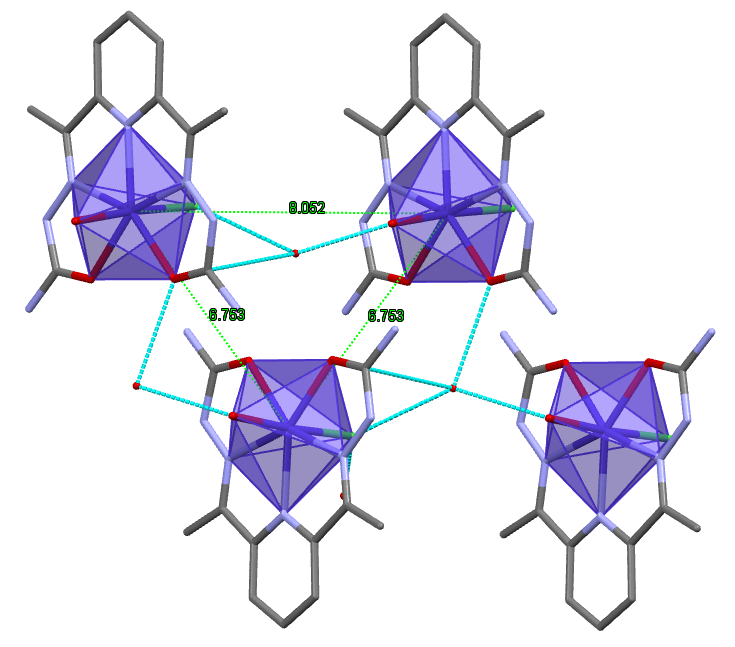
(a)

(b)

(c)

(d)

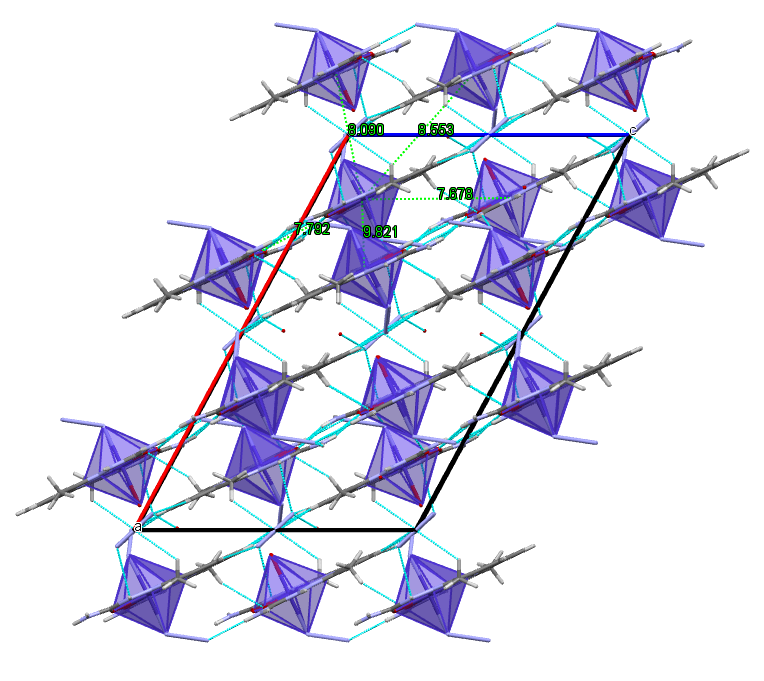
(e)

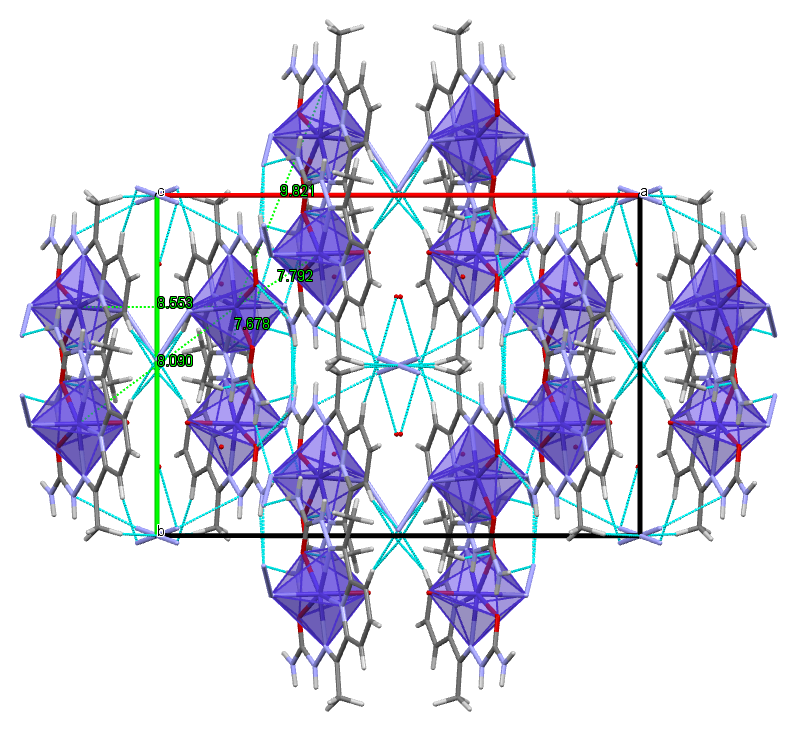
(f)

**Figure S1.** Fragments of crystal structures of **1** (a), **2** (b), **3** (c), **4** (d), **6** (e) and **7** (f). Dashed cyan and green lines show intermolecular H-bonds and intermolecular Co···Co separations (distances in Å), respectively. Disordering of solvate molecules and counterions is omitted for clarity.

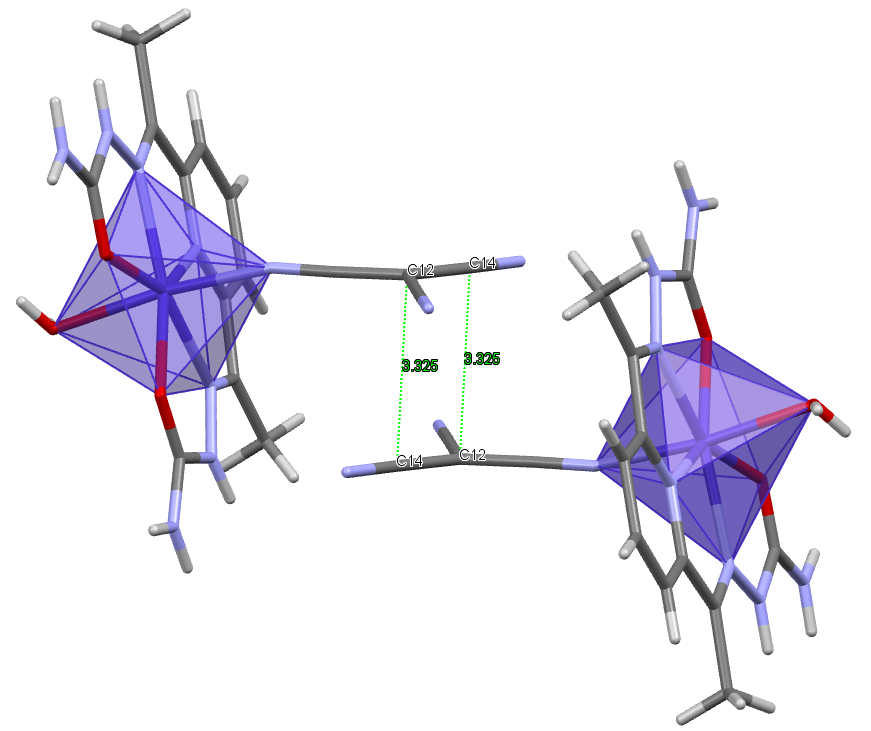
**Table S3.** Geometric parameters of H-bonds in crystal structures **1**− **5**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | D-H | d(D-H) | d(H..A) | <DHA | d(D..A) | A |
| **1** | N(8)-H(8A) | 0.860 | 2.11 | 155.1 | 2.91 | O(1) [ -x+1, -y+1, -z+1 ] |
| N(7)-H(7) | 0.860 | 2.50 | 159.3 | 3.32 | S(1) [ x-1, y, z ] |
| N(9)-H(9A) | 0.860 | 2.43 | 164.6 | 3.26 | N(2) [ -x, -y+1, -z+1 ] |
| N(6)-H(6) | 0.860 | 2.58 | 145.1 | 3.32 | S(2) [ x+1, y, z ] |
| O(3)-H(3A) | 0.820 | 2.72 | 134.1 | 3.34 | S(2) [ -x, -y+1, -z+1 ] |
| **2** | N(8)-H(8A) | 0.860 | 2.13 | 153.7 | 2.92 | O(1) [ -x+1, -y+1, -z+1 ] |
| N(7)-H(7) | 0.860 | 2.62 | 159.2 | 3.43 | Se(1) [ x-1, y, z ] |
| N(9)-H(9A) | 0.860 | 2.46 | 163.5 | 3.30 | N(2) [ -x, -y+1, -z+1 ] |
| N(6)-H(6) | 0.860 | 2.68 | 145.6 | 3.42 | Se(2) [ x+1, y, z ] |
| O(3)-H(3A) | 0.820 | 2.58 | 150.8 | 3.32 | Se(2) [ -x, -y+1, -z+1 ] |
| **3** | N(9)-H(9A) | 0.860 | 2.02 | 171.5 | 2.87 | O(2) [ -x+1, -y, -z ] |
| N(9)-H(9B) | 0.860 | 2.12 | 160.5 | 2.95 | N(11) [ -x, -y, -z ] |
| N(7)-H(7A) | 0.860 | 2.51 | 113.0 | 2.96 | O(1W) [ x, y-1, z ] |
| N(6)-H(6A) | 0.860 | 2.05 | 157.1 | 2.86 | O(1W) |
| N(8)-H(8A) | 0.860 | 2.16 | 175.3 | 3.02 | N(11) [ x+1, y, z ] |
| O(2W)-H(7) | 0.865 | 1.94 | 167.2 | 2.79 | N(13) [ x, y+1, z ] |
| O(1W)-H(10) | 0.798 | 2.01 | 171.8 | 2.80 | O(2W) |
| O(1W)-H(15) | 0.878 | 1.93 | 168.2 | 2.80 | N(12) [ -x, -y+1, -z+1 ] |
| O(2W)-H(18) | 0.833 | 1.98 | 172.5 | 2.81 | N(10) [ -x+1, -y+1, -z ] |
| 4 | N(9)-H(9A) | 0.860 | 2.19 | 150.1 | 2.97 | O(2) [ -x+1, -y, -z+1 ] |
| N(9)-H(9A) | 0.860 | 2.52 | 116.9 | 3.01 | O(1) [ -x+1, -y, -z+1 ] |
| N(9)-H(9B) | 0.860 | 2.07 | 171.5 | 2.92 | O(5) |
| N(7)-H(7A) | 0.860 | 2.18 | 136.2 | 2.87 | O(4) |
| N(6)-H(6A) | 0.860 | 2.02 | 148.4 | 2.79 | O(1W) [-x, y+1/2,-z+1/2] |
| N(8)-H(8A) | 0.860 | 2.15 | 161.7 | 2.97 | O(5) [ -x-1, -y+1, -z ] |
| N(8)-H(8B) | 0.860 | 2.20 | 145.1 | 2.94 | O(1W) [-x, y+1/2, -z+1/2 ] |
| O(3)-H(1) | 0.758 | 1.93 | 123.0 | 2.42 | O(2W) |
| O(3)-H(1) | 0.758 | 2.18 | 141.4 | 2.81 | O(6) [ -x-1, y+1/2, -z+1/2 ] |
| O(3)-H(2) | 0.803 | 1.95 | 168.0 | 2.74 | O(6) [ x, -y+1/2, z+1/2 ] |
| O(1W)-H(4) | 0.905 | 2.02 | 165.8 | 2.91 | N(11) |
| O(1W)-H(3) | 0.899 | 2.14 | 136.5 | 2.86 | O(2) [ -x, -y+1, -z ] |
| **5** | N(9)-H(9A) | 0.860 | 2.17 | 176.3 | 3.03 | N(13) [ x, -y, z+1/2 ] |
| N(9)-H(9B) | 0.860 | 2.30 | 151.5 | 3.09 | N(1) [-x+1/2,y+1/2,-z+1/2] |
| N(8)-H(8A) | 0.860 | 2.05 | 167.0 | 2.90 | O(1) [-x+1/2,-y-1/2,-z+1] |
| N(8)-H(8A) | 0.860 | 2.64 | 117.0 | 3.12 | O(2\_ [-x+1/2,-y-1/2,-z+1] |
| N(8)-H(8B) | 0.860 | 2.14 | 162.3 | 2.98 | N(13) [-x+1/2,y-1/2,-z+1/2] |
| N(7)-H(7A) | 0.860 | 1.96 | 164.2 | 2.79 | O(1W) [ -x+1, -y, -z+1 ] |
| O(1W)-H(1) | 0.891 | 2.01 | 165.0 | 2.88 | N(1) [ x+1/2, -y-1/2, z+1/2 ] |
| O(1W)-H(2) | 0.856 | 2.01 | 163.6 | 2.84 | O(2W) |
| O(2W)-H(3) | 1.003 | 1.88 | 177.7 | 2.88 | N(15) [ -x+1, -y-1, -z+1 ] |
| O(2W)-H(3) | 1.003 | 2.56 | 154.4 | 3.49 | N(14) |

*(a)*

*(b)*

**Figure S2.** Fragments of **5** crystal structure: *ac* projection (a) and*ab*projection (b). Dashed cyan and green lines show intermolecular H-bonds and intermolecular Co···Co separations (distances in Å), respectively.



**Figure S3.** Stacking interactions of tcm ligands of adjacent molecules in the crystal structure of **4**.

|  |  |
| --- | --- |
| **1** | **5** |
| **Figure S4** The *DC* field-dependencies of AC susceptibility (χ″) at 2.0 K and two frequencies (100 Hz, 1000 Hz) for **1** and **5.** | |

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
| (a) | | (b) | |
|  |  |  |  |
| (c) | | (d) | |
|  |  |  |  |
| (e) | | (f) | |
|  | |  | |
| *(g)* | | | |

**Figure S5** Argand (Cole−Cole) plots from 2 to 7 K and Arrhenius plots of relaxation times as ln(τ) vs. 1/T under DC ﬁelds for **1** (a), **2**(b), **3** (c), **4** (d), **5** (e), **6** (f) and **7** (g). Empty circles - experimental data, solid lines - fit data within the two-component generalized Debye model with parameters listed in Tables S4-S10. Solid line represents the graph of eqn 2 (in main text) with best-ﬁt parameters (see the Table S11).

**Table S4**. Best fit parameters of the generalized Debye model for the Cole-Cole plot of complex **1** at *HDC* = 1.0kOe

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *T*, K | *χ*S, cm3 mol–1 | Δ*χ*T, cm3 mol–1 | *τ*, s | *α* | *R1 a* |
| 2.0 | 0.053 | 0.296 | 1.04E-04 | 0.442 | 3.22E-04 |
| 2.25 | 0.061 | 0.286 | 1.12E-04 | 0.427 | 3.46E-04 |
| 2.5 | 0.061 | 0.279 | 1.11E-04 | 0.435 | 2.51E-04 |
| 2.75 | 0.065 | 0.269 | 1.11E-04 | 0.417 | 3.75E-04 |
| 3.0 | 0.068 | 0.264 | 1.12E-04 | 0.406 | 4.58E-04 |
| 3.25 | 0.067 | 0.257 | 1.06E-04 | 0.404 | 5.64E-04 |
| 3.5 | 0.067 | 0.246 | 1.01E-04 | 0.391 | 3.91E-04 |
| 4.0 | 0.072 | 0.236 | 1.08E-04 | 0.361 | 5.39E-04 |
| 4.25 | 0.072 | 0.223 | 0.98E-04 | 0.327 | 3.54E-04 |
| 4.5 | 0.073 | 0.216 | 0.94E-04 | 0.300 | 4.09E-04 |
| 4.75 | 0.072 | 0.212 | 0.91E-04 | 0.299 | 3.49E-04 |
| 5.5 | 0.071 | 0.191 | 0.65E-04 | 0.197 | 1.98E-04 |
| 6.0 | 0.068 | 0.178 | 0.44E-04 | 0.134 | 9.56E-05 |
| 6.5 | 0.066 | 0.168 | 0.30E-04 | 0.072 | 6.75E-05 |
| 7.0 | 0.062 | 0.160 | 0.17E-04 | 0.039 | 1.61E-05 |

*a* The mean residual sum of squares, *R*1 = .

**Table S5**. Best fit parameters of the generalized Debye model for the Cole-Cole plot of complex **2** at *HDC* = 1.5kOe

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *T*, K | *χ*S, cm3 mol–1 | Δ*χ*T, cm3 mol–1 | *τ*, s | *α* | *R*1*a* |
| 2.0 | 0.027 | 0.416 | 5.49E-04 | 0.242 | 1.15E-02 |
| 2.25 | 0.028 | 0.385 | 4.99E-04 | 0.224 | 3.62E-03 |
| 2.5 | 0.028 | 0.351 | 4.43E-04 | 0.208 | 1.60E-03 |
| 2.75 | 0.027 | 0.323 | 3.98E-04 | 0.200 | 2.28E-03 |
| 3.0 | 0.026 | 0.302 | 3.62E-04 | 0.197 | 2.51E-03 |
| 3.25 | 0.026 | 0.280 | 3.21E-04 | 0.182 | 2.75E-03 |
| 3.5 | 0.026 | 0.262 | 2.88E-04 | 0.176 | 2.40E-03 |
| 3.75 | 0.025 | 0.246 | 2.58E-04 | 0.172 | 2.09E-03 |
| 4.0 | 0.025 | 0.226 | 2.24E-04 | 0.151 | 3.69E-03 |
| 4.25 | 0.025 | 0.217 | 2.02E-04 | 0.145 | 3.89E-03 |
| 4.5 | 0.024 | 0.207 | 1.80E-04 | 0.146 | 2.80E-03 |
| 4.75 | 0.024 | 0.196 | 1.58E-04 | 0.132 | 1.76E-03 |
| 5.0 | 0.024 | 0.186 | 1.38E-04 | 0.120 | 2.37E-03 |
| 6.0 | 0.023 | 0.156 | 0.71E-04 | 0.067 | 1.19E-03 |
| 7.0 | 0.023 | 0.135 | 0.24E-04 | 0.013 | 2.11E-03 |

a The mean residual sum of squares, R1 = .

**Table S6**. Best fit parameters of the generalized Debye model for the Cole-Cole plot of complex **3** at *HDC* = 1.2kOe

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *T*, K | *χ*S, cm3 mol–1 | Δ*χ*T, cm3 mol–1 | *τ*, s | *α* | *R*1*a* |
| 2.0 | 0.047 | 0.480 | 2.70E-03 | 0.128 | 2.09E-03 |
| 2.25 | 0.047 | 0.467 | 2.35E-03 | 0.126 | 1.65E-03 |
| 2.5 | 0.045 | 0.452 | 2.05E-03 | 0.118 | 1.88E-03 |
| 2.75 | 0.045 | 0.443 | 1.90E-03 | 0.117 | 1.46E-03 |
| 3.0 | 0.044 | 0.427 | 1.630E-03 | 0.104 | 1.74E-03 |
| 3.25 | 0.044 | 0.418 | 1.400E-03 | 0.099 | 1.00E-03 |
| 3.5 | 0.043 | 0.408 | 1.22E-03 | 0.099 | 1.22E-03 |
| 3.75 | 0.043 | 0.392 | 1.01E-03 | 0.077 | 1.07E-03 |
| 4.0 | 0.040 | 0.384 | 0.86E-03 | 0.095 | 0.64E-03 |
| 4.25 | 0.039 | 0.372 | 0.67E-03 | 0.093 | 0.63E-03 |
| 4.5 | 0.038 | 0.365 | 0.56E-03 | 0.096 | 0.39E-03 |
| 4.75 | 0.035 | 0.352 | 0.41E-03 | 0.106 | 0.87E-03 |
| 5.0 | 0.033 | 0.341 | 0.31E-03 | 0.108 | 0.48E-03 |

*a* The mean residual sum of squares, *R*1 = .

**Table S7**. Best fit parameters of the generalized Debye model for the Cole-Cole plot of complex **4** at *HDC* = 1.5kOe

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *T*, K | *χ*S, cm3 mol–1 | Δ*χ*T1, cm3 mol–1 | *τ1*, s | *α1* | Δ*χ*T2, cm3 mol–1 | *τ2*, s | *α2* | *R*1*a* |
| 2.0 | 0.142 | 0.233 | 2.96E-05 | 0.254 | 0.720 | 2.87E-03 | 0.437 | 3.81E-04 |
| 2.25 | 0.087 | 0.364 | 3.05E-05 | 0.434 | 0.510 | 2.59E-03 | 0.326 | 3.73E-04 |
| 2.5 | 0.076 | 0.343 | 2.55E-05 | 0.449 | 0.462 | 2.05E-03 | 0.297 | 3.19E-04 |
| 2.75 | 0.045 | 0.399 | 2.74E-05 | 0.532 | 0.366 | 1.73E-03 | 0.232 | 3.74E-04 |
| 3.0 | 0.058 | 0.345 | 2.54E-05 | 0.510 | 0.345 | 1.38E-03 | 0.207 | 3.66E-04 |
| 3.25 | 0.065 | 0.308 | 2.37E-05 | 0.501 | 0.324 | 1.11E-03 | 0.185 | 4.65E-04 |
| 3.5 | 0.085 | 0.253 | 2.43E-05 | 0.454 | 0.312 | 9.05E-04 | 0.165 | 5.06E-04 |
| 3.75 | 0.097 | 0.218 | 2.57E-05 | 0.421 | 0.293 | 7.41E-04 | 0.141 | 5.15E-04 |
| 4.0 | 0.108 | 0.190 | 2.80E-05 | 0.387 | 0.275 | 6.16E-04 | 0.119 | 4.79E-04 |
| 4.25 | 0.111 | 0.165 | 2.66E-05 | 0.359 | 0.264 | 5.03E-04 | 0.106 | 3.90E-04 |
| 4.5 | 0.111 | 0.146 | 2.41E-05 | 0.341 | 0.256 | 4.12E-04 | 0.101 | 2.47E-04 |
| 4.75 | 0.111 | 0.132 | 2.33E-05 | 0.322 | 0.243 | 3.39E-04 | 0.085 | 2.02E-04 |
| 5.0 | 0.110 | 0.118 | 2.12E-05 | 0.300 | 0.236 | 2.77E-04 | 0.076 | 2.78E-04 |
| 6.0 | 0.125 | 0.135 | 5.13E-05 | 0.175 | 0.132 | 1.31E-04 | 0.0 | 1.82E-04 |
| 7.0 | 0.090 | 0.071 | 7.31E-06 | 0.147 | 0.178 | 3.81E-05 | 0.0 | 1.33E-04 |

*a* The mean residual sum of squares, *R*1 = .

**Table S8**. Best fit parameters of the generalized Debye model for the Cole-Cole plot of complex **5** at *HDC* = 1.8kOe

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *T*, K | *χ*S, cm3 mol–1 | Δ*χ*T, cm3 mol–1 | *τ*, s | *α* | *R*1*a* |
| 2.0 | 0.176 | 1.028 | 4.56E-04 | 0.060 | 0.21E-02 |
| 2.25 | 0.174 | 1.030 | 4.39E-04 | 0.054 | 2.71E-03 |
| 2.5 | 0.169 | 1.035 | 4.26E-04 | 0.050 | 2.14E-03 |
| 2.75 | 0.157 | 1.039 | 3.93E-04 | 0.062 | 2.68E-03 |
| 3.0 | 0.155 | 1.031 | 3.70E-04 | 0.052 | 1.47E-03 |
| 3.25 | 0.146 | 1.023 | 3.27E-04 | 0.056 | 8.57E-04 |
| 3.5 | 0.142 | 0.990 | 2.82E-04 | 0.055 | 1.40E-03 |
| 3.75 | 0.141 | 0.956 | 2.52E-04 | 0.041 | 8.76E-04 |
| 4.0 | 0.135 | 0.933 | 2.25E-04 | 0.042 | 1.71E-03 |
| 4.25 | 0.131 | 0.897 | 1.92E-04 | 0.040 | 1.54E-03 |
| 4.5 | 0.127 | 0.860 | 1.63E-04 | 0.037 | 9.77E-04 |
| 4.75 | 0.124 | 0.831 | 1.43E-04 | 0.034 | 6.91E-04 |
| 5.0 | 0.120 | 0.803 | 1.23E-04 | 0.040 | 6.40E-04 |
| 6.0 | 0.111 | 0.700 | 7.18E-05 | 0.028 | 3.64E-04 |
| 7.0 | 0.107 | 0.616 | 3.58E-05 | 0.016 | 2.33E-04 |

*a* The mean residual sum of squares, *R*1 = .

**Table S9**. Best fit parameters of the generalized Debye model for the Cole-Cole plot of complex **6** at *HDC* = 1.2kOe

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *T*, K | *χ*S, cm3 mol–1 | Δ*χ*T, cm3 mol–1 | *τ*, s | *α* | *R*1*a* |
| 2.0 | 0.314 | 0.852 | 0.658E-03 | 0.215 | 0.119E-01 |
| 2.25 | 0.283 | 0.814 | 0.560E-03 | 0.175 | 0.604E-02 |
| 2.5 | 0.257 | 0.773 | 0.476E-03 | 0.148 | 0.255E-02 |
| 2.75 | 0.236 | 0.734 | 0.410E-03 | 0.131 | 0.102E-02 |
| 3.0 | 0.219 | 0.695 | 0.354E-03 | 0.119 | 0.432E-03 |
| 3.25 | 0.203 | 0.657 | 0.306E-03 | 0.113 | 0.226E-03 |
| 3.5 | 0.190 | 0.620 | 0.265E-03 | 0.107 | 0.237E-03 |
| 3.75 | 0.179 | 0.586 | 0.230E-03 | 0.109 | 0.161E-03 |
| 4.0 | 0.169 | 0.555 | 0.200E-03 | 0.097 | 0.164E-03 |
| 4.25 | 0.161 | 0.526 | 0.175E-03 | 0.092 | 0.165E-03 |
| 4.5 | 0.153 | 0.500 | 0.154E-03 | 0.088 | 0.131E-03 |
| 4.75 | 0.147 | 0.476 | 0.135E-03 | 0.082 | 0.121E-03 |
| 5.0 | 0.141 | 0.454 | 0.119E-03 | 0.077 | 0.101E-03 |
| 7.0 | 0.110 | 0.332 | 0.359E-04 | 0.029 | 0.361E-04 |

*a* The mean residual sum of squares, *R*1 = .

**Table S10**. Best fit parameters of the generalized Debye model for the Cole-Cole plot of complex **7** at *HDC* = 1.4kOe

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *T*, K | *χ*S, cm3 mol–1 | Δ*χ*T, cm3 mol–1 | *τ*, s | *α* | *R*1*a* |
| 2.0 | 0.102 | 0.83 | 2.54E-03 | 0.34 | 2.87E-03 |
| 2.25 | 0.097 | 0.79 | 2.12E-03 | 0.30 | 1.78E-03 |
| 2.5 | 0.093 | 0.74 | 1.79E-03 | 0.26 | 1.12E-03 |
| 2.75 | 0.088 | 0.70 | 1.52E-03 | 0.24 | 8.32E-03 |
| 3.0 | 0.084 | 0.65 | 1.30E-03 | 0.22 | 3.49E-04 |
| 3.25 | 0.081 | 0.61 | 1.12E-03 | 0.20 | 1.79E-04 |
| 3.5 | 0.077 | 0.57 | 9.44E-04 | 0.17 | 3.34E-04 |
| 3.75 | 0.074 | 0.55 | 8.31E-04 | 0.16 | 8.48E-05 |
| 4.0 | 0.072 | 0.52 | 7.22E-04 | 0.15 | 1.13E-04 |
| 4.25 | 0.069 | 0.49 | 6.30E-04 | 0.14 | 1.35E-04 |
| 4.5 | 0.067 | 0.47 | 5.41E-04 | 0.13 | 1.03E-04 |
| 4.75 | 0.066 | 0.45 | 4.65E-04 | 0.12 | 1.34E-04 |
| 5.0 | 0.064 | 0.43 | 3.96E-04 | 0.10 | 1.66E-04 |
| 5.25 | 0.062 | 0.41 | 3.34E-04 | 0.09 | 3.50E-04 |
| 5.5 | 0.061 | 0.39 | 2.79E-04 | 0.08 | 2.41E-04 |
| 6.0 | 0.058 | 0.36 | 1.88E-04 | 0.06 | 0.97E-04 |
| 6.5 | 0.055 | 0.33 | 1.21E-04 | 0.04 | 2.72E-04 |
| 7.0 | 0.053 | 0.31 | 7.57E-05 | 0.03 | 1.01E-04 |
| 7.5 | 0.050 | 0.29 | 4.41E-05 | 0.02 | 2.13E-04 |
| 8.0 | 0.050 | 0.27 | 2.57E-05 | 0.02 | 0.85E-04 |

*a* The mean residual sum of squares, *R*1 = .

**Table S11**. Crystal data and structure refinement for **1**– **5**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **1** | **2** | **3** | **4** | **5** |
| formula (M) | C14H18Co1N9O2.5S2  (475.43) | C14H18Co1N9O2.5Se2  (569.23) | C15H19Co1N13O4  (504.36) | C15H19Co1N11O7.16  (526.92) | C22H40Co2N26O9  (928.64) |
| Temperature, K | 150.0(1) | 150.0(1) | 100.0(2) | 150.0(1) | 150.0(1) |
| Crystal system | monoclinic | monoclinic | triclinic | monoclinic | monoclinic |
| space group | P21/c | P21/c | P-1 | P21/c | С2/c |
| a, Å | 7.8463(3) | 7.9941(3) | 8.7403(4) | 11.8562(4) | 22.3521(7) |
| b, Å | 16.9377(6) | 17.2119(5) | 11.0815(4) | 15.6902(7) | 13.8512(4) |
| c, Å | 15.0047(5) | 15.0758(5) | 11.7571(5) | 11.9620(3) | 13.9977(4) |
| α,° | 90 | 90 | 76.022(3) | 90 | 90 |
| β,° | 103.360(3) | 103.260(3) | 71.082(4) | 94.515(3) | 118.433(3) |
| γ,° | 90 | 90 | 76.159(3) | 90 | 90 |
| Volume, Å3 | 1940.1(1) | 2019.0(1) | 1029.15(7) | 2218.3(1) | 3811.0(2) |
| Z, ρcalc, g/cm3 | 4, 1.628 | 4, 1.873 | 2, 1.628 | 4, 1.578 | 4, 1.619 |
| µ, mm-1 | 1.135 | 4.489 | 0.890 | 0.837 | 0.955 |
| F(000) | 976 | 1120 | 518 | 1081 | 1912 |
| Crystal size, mm3 | 0.35×0.2×0.15 | 0.3×0.15×0.1 | 0.3×0.15×0.1 | 0.4×0.3×0.2 | 0.3×0.2×0.1 |
| θ range, ° | 2.78 - 29.07 | 3.02 - 29.07 | 2.88 - 26.32 | 2.83 - 29.07 | 2.94 - 26.32 |
| Index ranges | -7 ≤ h ≤ 10,  -23 ≤ k ≤ 21,  -20 ≤ l ≤ 20 | -10 ≤ h ≤ 10,  -23 ≤ k ≤ 12,  -20 ≤ l ≤ 18 | -10 ≤ h ≤ 10,  -12 ≤ k ≤ 13,  -14≤ l ≤ 12 | -16 ≤ h ≤ 16,  -13 ≤ k ≤ 21,  -15≤ l ≤ 16 | -16 ≤ h ≤ 27,  -17 ≤ k ≤ 14,  -17≤ l ≤ 16 |
| Reflections collected / unique [R(int)] | 10135 / 5189  [0.0227] | 10204 / 5397  [0.0236] | 7537 / 4171  [0.0265] | 11149 / 5929  [0.0282] | 7984 / 3882 [0.0256] |
| Completeness to θ | 0.999 | 0.998 | 0.998 | 0.999 | 0.999 |
| Number of parameters | 275 | 272 | 314 | 329 | 289 |
| GOOF | 1.051 | 1.032 | 1.033 | 1.042 | 1.064 |
| Final R indices [I>2σ(I)] | R1 = 0.0351,  wR2 = 0.0824 | R1 = 0.0354,  wR2 = 0.0742 | R1 = 0.0361,  wR2 = 0.0787 | R1 = 0.0534,  wR2 = 0.1334 | R1 = 0.0402,  wR2 = 0.1005 |
| R indices (all data) | R1 = 0.0452,  wR2 = 0.0891 | R1 = 0.0538  wR2 = 0.0805 | R1 = 0.0477  wR2 = 0.0838 | R1 = 0.0693  wR2 = 0.1494 | R1 = 0.0545  wR2 = 0.1064 |
| Δρmax / Δρmin, e·Å-3 | 0.503 / -0.540 | 0.719 /-0.822 | 0.478 /-0.552 | 1.010 / -0.782 | 0.886 / -0.604 |
| *CCDC* number | 1952369 | 1952371 | 1952370 | 1952373 | 1952372 |

**Table S12**. Magnetic anisotropy parameters (*D* parameters) for seven-coordinated Co(II) complexes with the 2,6-diacethylpyridine-based opened acyclic ligands (Figure **1**, main text)

|  |  |  |  |
| --- | --- | --- | --- |
| No | Compound | *D*(cm-1) | Ref. |
| **1** | [Co(H2dapsc)(SCN)2]∙0.5C2H5OH | 35.6 | This work |
| **2** | [Co(H2dapsc)(SeCN)2]∙0.5C2H5OH | 38.20 | This work |
| **3** | [Co(H2dapsc)(N(CN)2)2]∙2H2O | 35.3 | This work |
| **4** | [Co(H2dapsc)(C(CN)3)(H2O)](NO3)∙1.16H2O | 33.60 | This work |
| **5** | {[Co(H2dapsc)(H2O)(N3)][Co(H2dapsc)(N3)2]}N3⋅4H2O | 40.4 | This work |
| **6** | [Co(H2dapsc)(H2O)2)](NO3)2∙2H2O | 38.02 | This work |
| **7** | [Co(H2dapsc)(Cl)(H2O)]Cl∙2H2O | 35.61 | This work |
| **8** | [Co(H2dapbh)(H2O)(NO3)](NO3) | 32.4 | 1,2 |
| **9** | [Co(H2dapbh)I(H2O)]I∙H2O | 30.0 | 3 |
| **10** | [Co(H2dapbh)Br(H2O)]Br∙H2O | 30.0 | 3 |
| **11** | [Co(dapbh)(im)2]·H2O | 24.8 | 2 |
| **12** | [Co(H2dapbh)(SCN)2] | 15.9 | 4 |
| **13** | [Co(H2daps)(MeOH)2] | 43.1 | 5 |
| **14** | [Co(H4daps)(NCS)(MeOH)]·(ClO4)·(MeOH) | 41.5 | 5 |
| **15** | [Co(H4daps)(NCS)2]·(MeOH)2 | 38.8 | 5 |

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