**Supplementary Information**

# Transition-metal(II) complexes with a tripodal hexadentate ligand, 1,1,1-tris[2-aza-3-(imidazol-4-yl)prop-2-enyl]ethane, exhibiting incomplete total or absolute spontaneous resolution

Misaki Matsushima,[a] Koki Wada,[a] Yuki Horino,[a] Kazuma Takahara,[a] Yukinari Sunatsuki [a] and Takayoshi Suzuki *[ab]

[a] Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan.

[b] Research Institute for Interdisciplinary Science, Okayama University, Okayama 700-8530, Japan.

E-mail: suzuki@okayama-u.ac.jp

**Contents:**

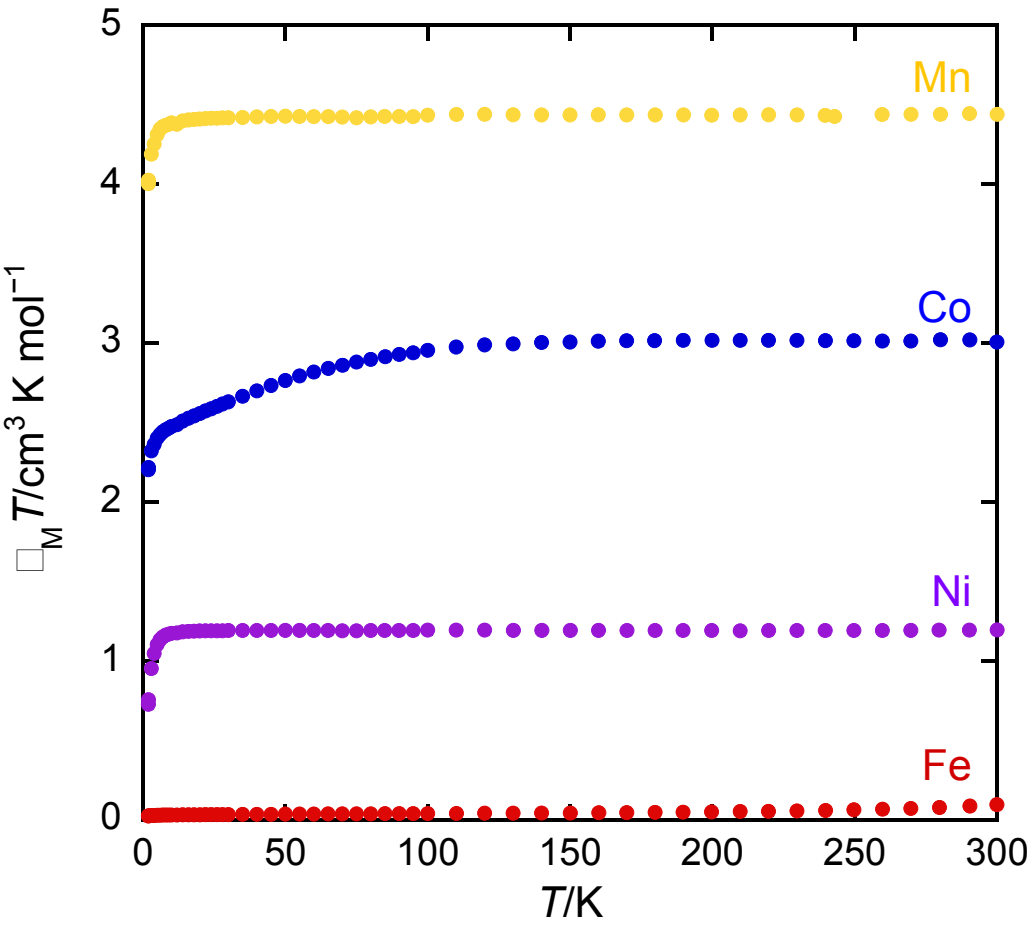
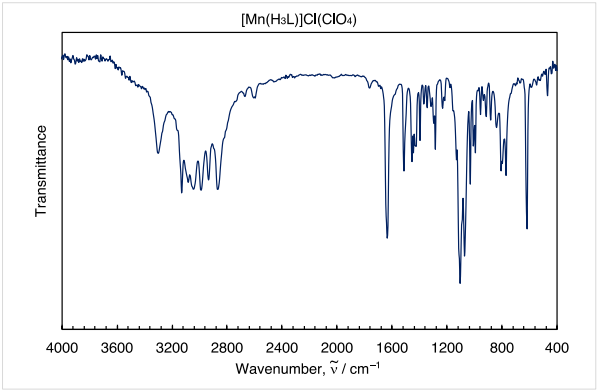
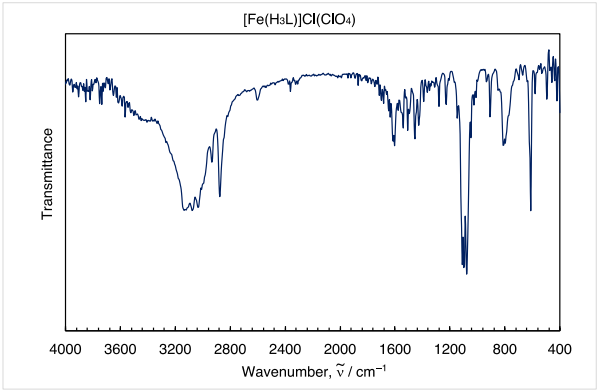



**Fig. S1** Temperature-dependence of the magnetic susceptibility, $\chi_M T$ vs. $T$ plots of $[Mn(H_3L)]Cl(ClO_4)$ (**1**: yellow), (*b*) $[Fe(H_3L)]Cl(ClO_4)$ (**2**: red), (*c*) $[Co(H_3L)]Cl(ClO_4)$ (**3**: blue) and $[Ni(H_3L)]Cl(ClO_4)$ (**4**: purple).

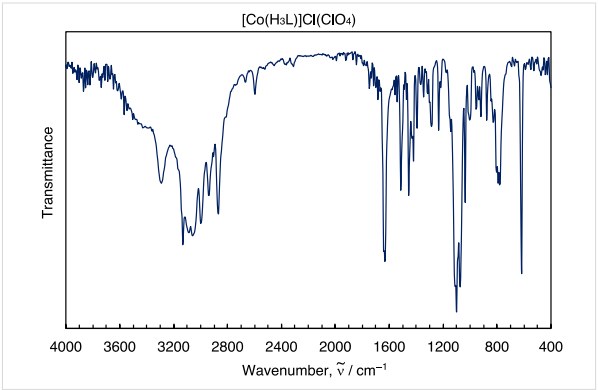
(*a*)



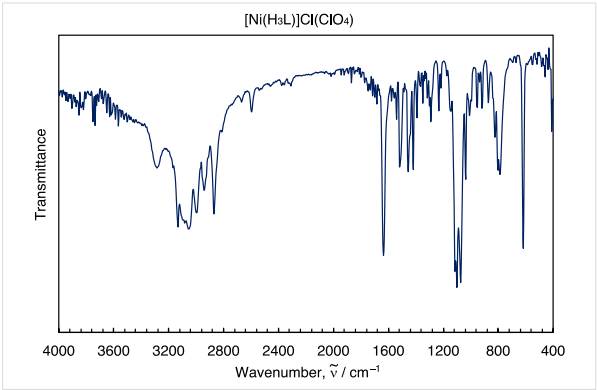

(*b*)




(*c*)




(*d*)




(*e*)

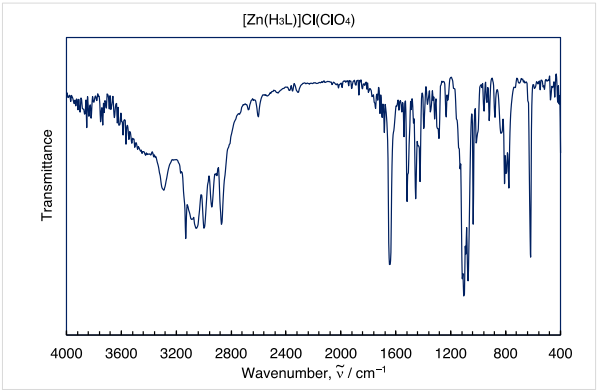



**Fig. S2** FT-IR spectra of (*a*) $[Mn(H_3L)]Cl(ClO_4)$ (**1**), (*b*) $[Fe(H_3L)]Cl(ClO_4)$ (**2**), (*c*) $[Co(H_3L)]Cl(ClO_4)$ (**3**), (*d*) $[Ni(H_3L)]Cl(ClO_4)$ (**4**) and (*e*) $[Zn(H_3L)]Cl(ClO_4)$ (**5**).

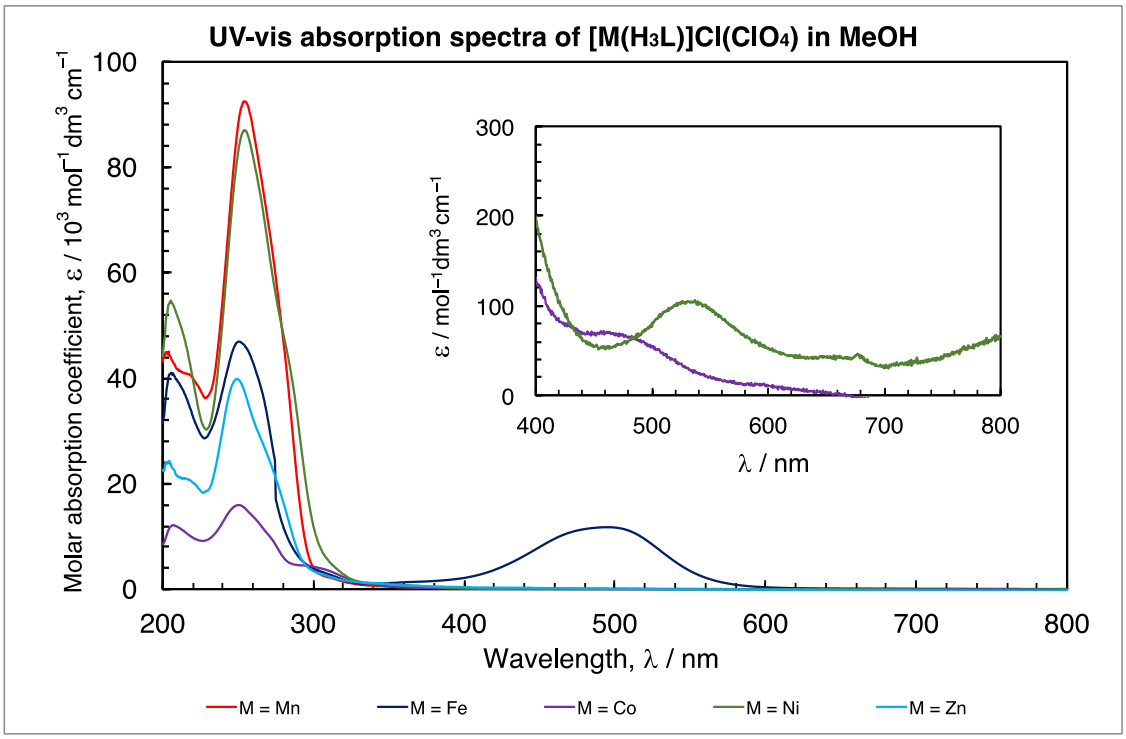



**Fig. S3** UV-vis absorption spectra of (*a*) $[Mn(H_3L)]Cl(ClO_4)$ (**1**: red), (*b*) $[Fe(H_3L)]Cl(ClO_4)$ (**2**: dark blue), (*c*) $[Co(H_3L)]Cl(ClO_4)$ (**3**: purple), (*d*) $[Ni(H_3L)]Cl(ClO_4)$ (**4**: green) and (*e*) $[Zn(H_3L)]Cl(ClO_4)$ (**5**: sky blue) in methanol.

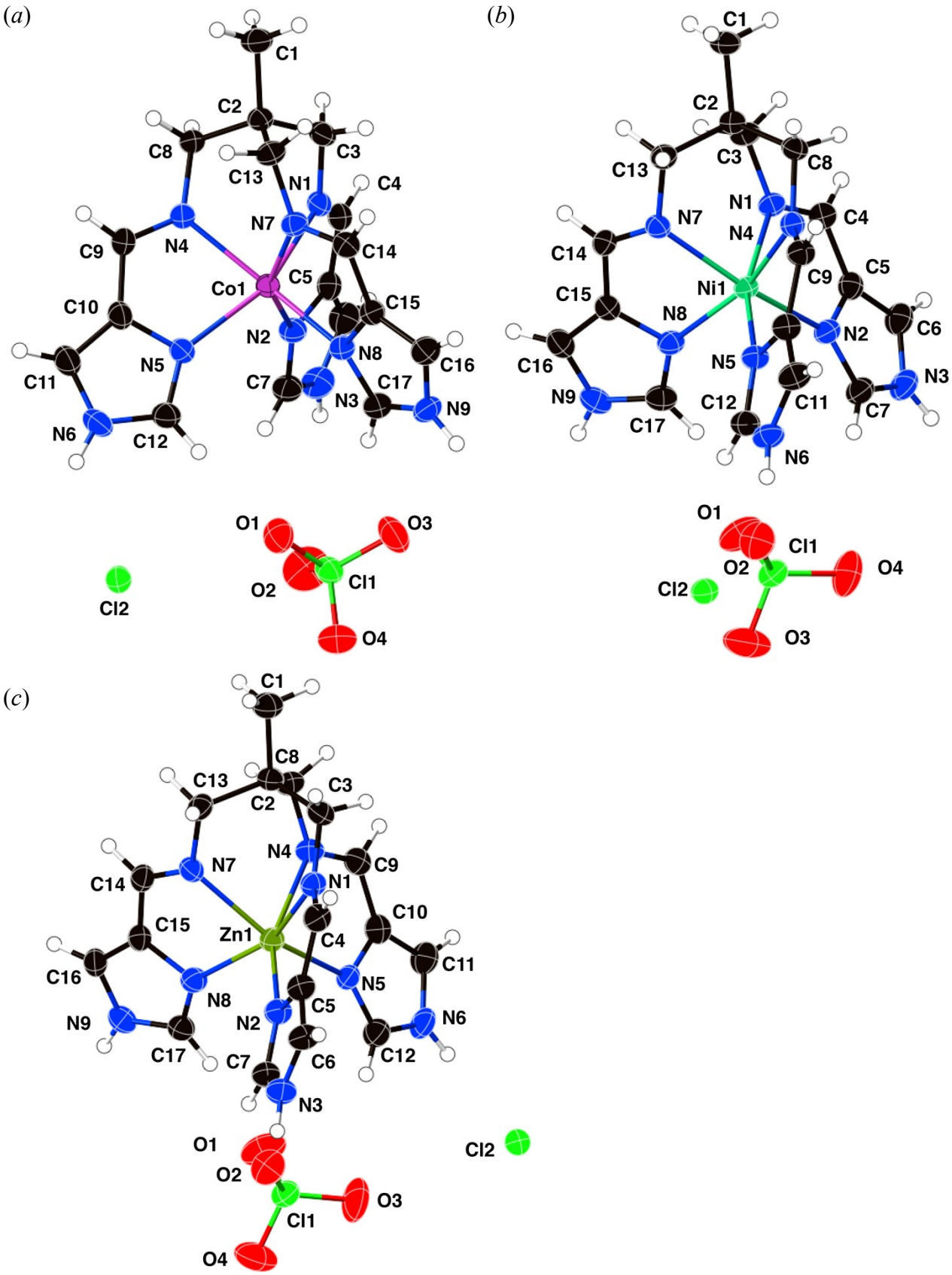



**Fig. S4** ORTEP drawings (50% probability level) of (*a*) $[Co(H_3L)]Cl(ClO_4)$ (**3**), (*b*) $[Ni(H_3L)]Cl(ClO_4)$ (**4**) and (*c*) $[Zn(H_3L)]Cl(ClO_4)$ (**5**) with atom-numbering schemes.

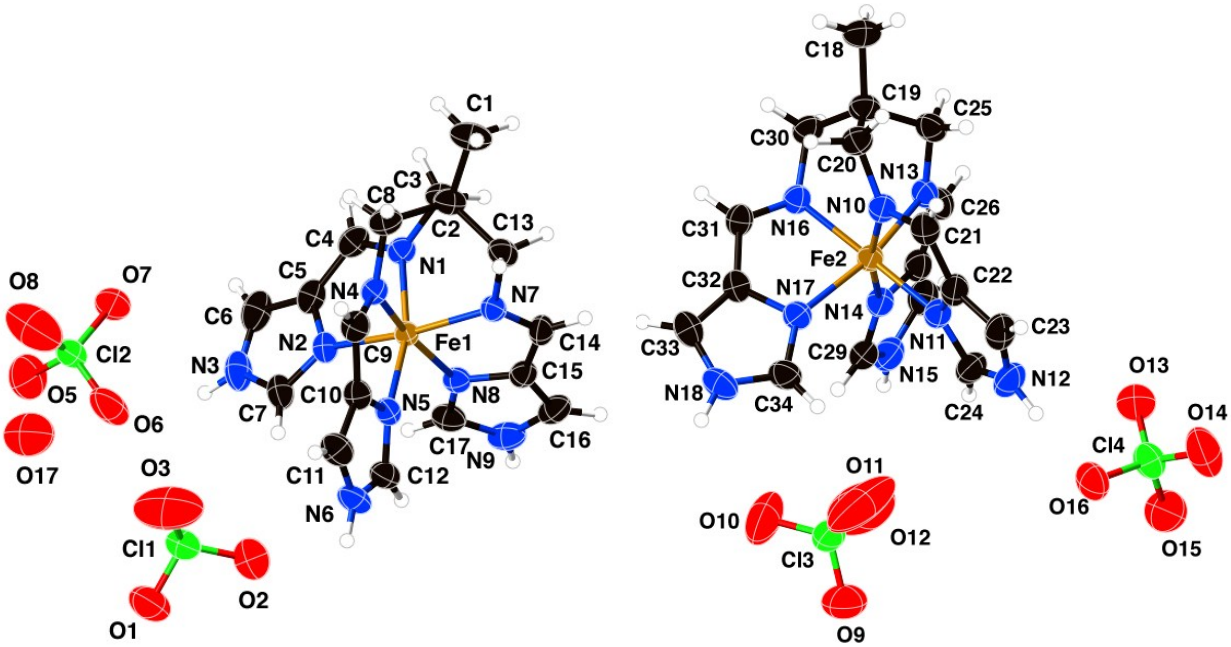



**Fig. S5** An ORTEP drawing (50% probability level) of crystallographically independent complex cations, counter anions, and a hydrated water molecules in $[Fe(H_3L)](ClO_4)_2 \cdot 0.5H_2O$ (**2A**) with atom-numbering schemes.

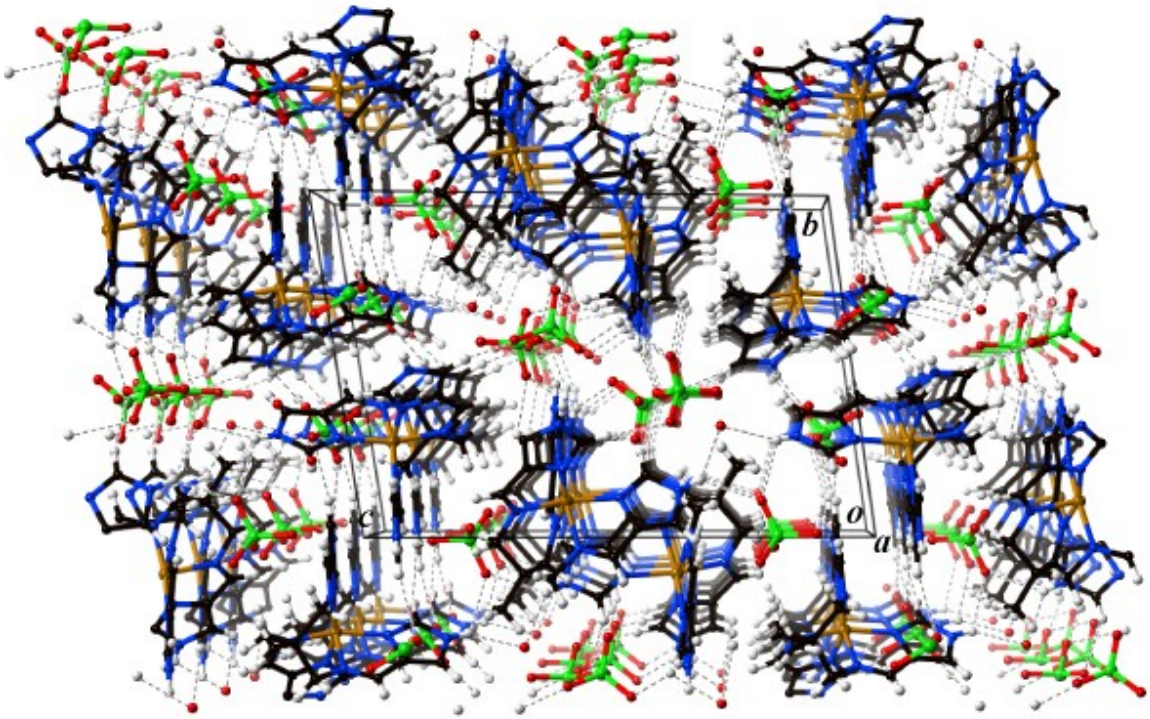



**Fig. S6** A packing diagram viewed along the *a* axis of $[Fe(H_3L)](ClO_4)_2 \cdot 0.5H_2O$ (**2A**).

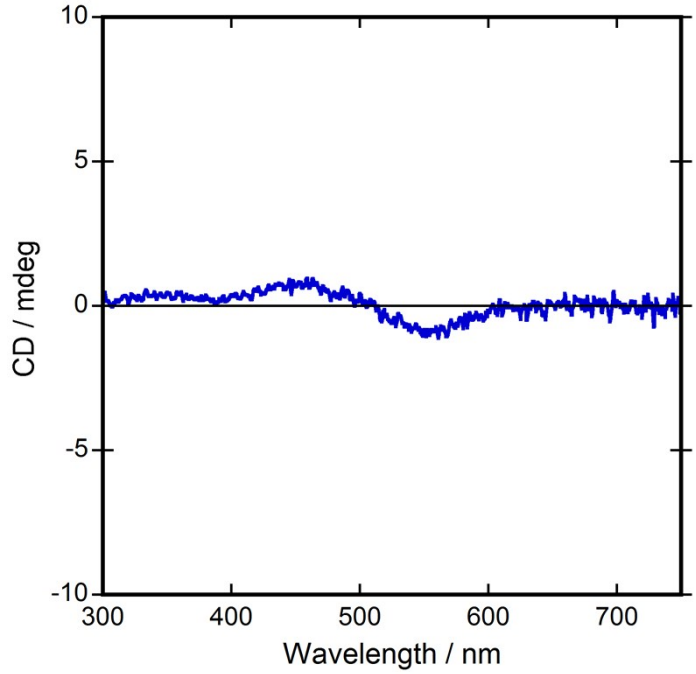
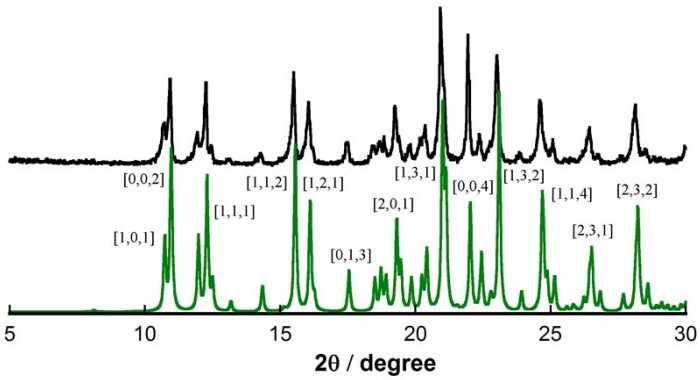
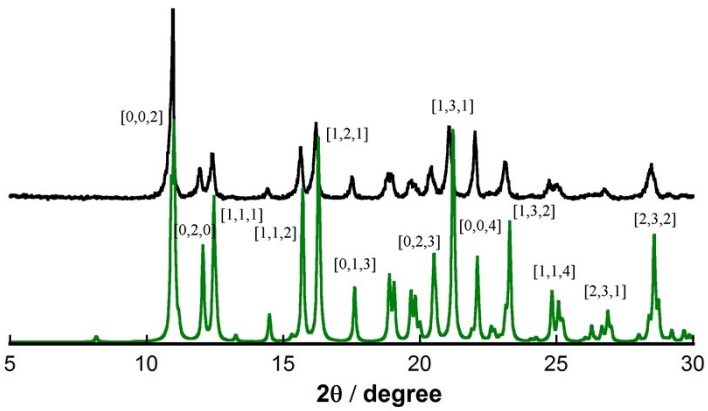



**Fig. S7** A CD spectrum of a methanol solution dissolving a piece of single-crystal of $[Fe(H_3L)]Cl(ClO_4)$ (**2**).

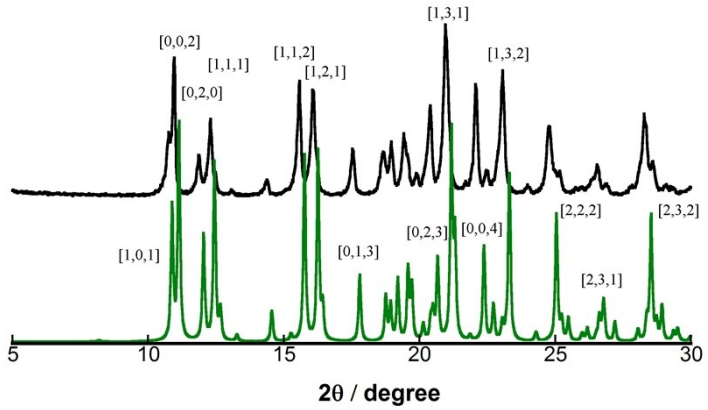
(*a*)




(*b*)




(*c*)




(*d*)

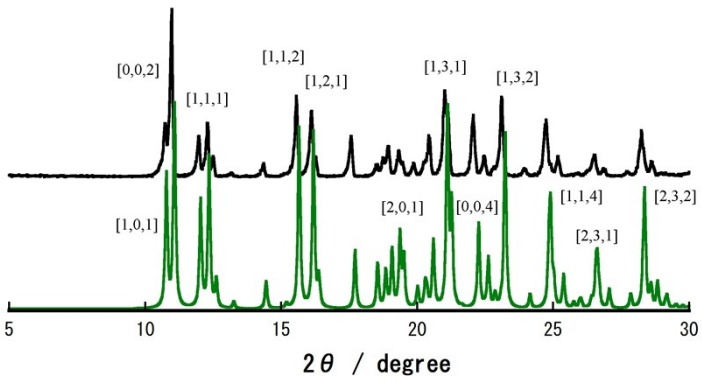



**Fig. S8** The observed powder X-ray diffraction (PXRD) spectra (upper, black) of the micro-crystalline samples obtained by recrystallisation and the simulated PXRD pattern (lower, green) from the single-crystal X-ray analyses for $[M(H_3L)]Cl(ClO_4)$ (M = Mn (*a*), Fe (*b*), Ni (*c*) and Zn (*d*).

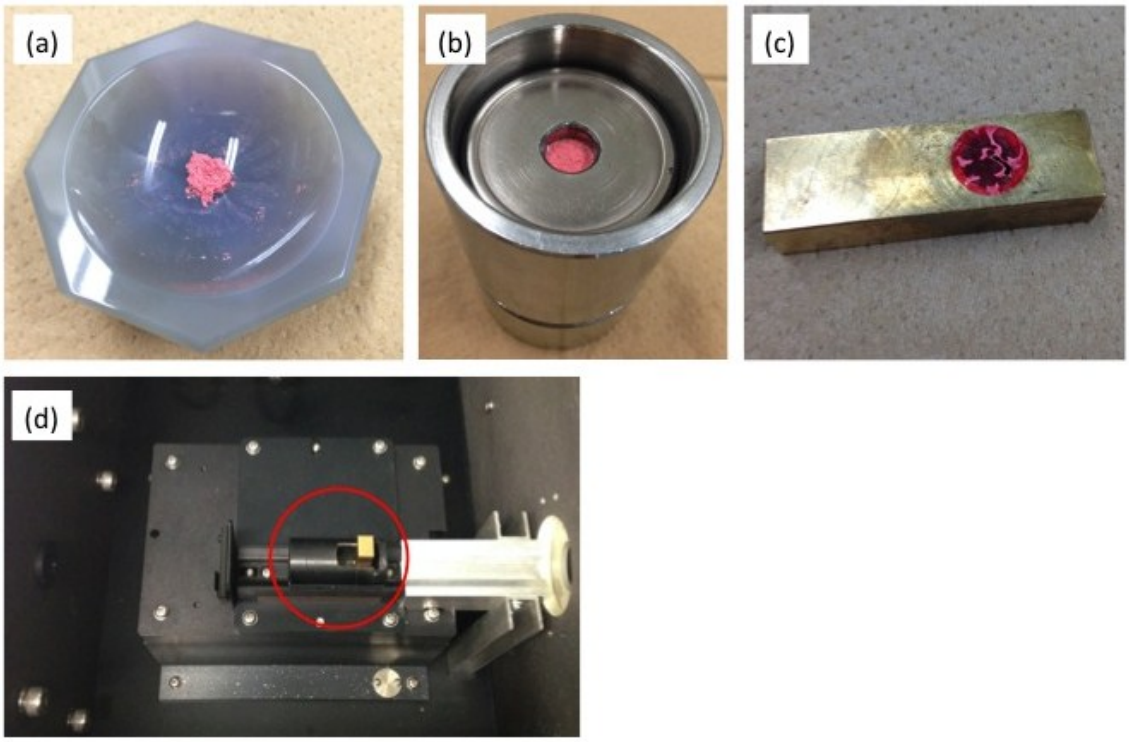



**Fig. S9** Preparation of a sample disk for solid-state CD measurement. A mixture of sample and KBr was well ground in an agate mortar (*a*) then vacuum pressed (*b*) to form a uniform disk. The disk was placed in a sample holder (*c*), which was then positioned in the cell holder of the spectropolarimeter (*d*).

**Table S1** Crystallographic data for compounds **1**–**5**.

| Complex | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| | $[Mn(H_3L)]Cl(ClO_4)$ | $[Fe(H_3L)]Cl(ClO_4)$ | $[Co(H_3L)]Cl(ClO_4)$ | $[Ni(H_3L)]Cl(ClO_4)$ | $[Zn(H_3L)]Cl(ClO_4)$ |
| Chemical formula | $C_{17}H_{21}Cl_2MnN_9O_4$ | $C_{17}H_{21}Cl_2FeN_9O_4$ | $C_{17}H_{21}Cl_2CoN_9O_4$ | $C_{17}H_{21}Cl_2N_9NiO_4$ | $C_{17}H_{21}Cl_2N_9O_4Zn$ |
| Formula weight | 541.25 | 542.18 | 545.26 | 545.04 | 551.70 |
| $T$ / K | 192(2) | 193(2) | 192(2) | 192(2) | 192(2) |
| Crystal color and shape | yellow, platelet | red, platelet | brown, platelet | purple, platelet | colorless, block |
| Size of specimen / mm | 0.5 × 0.3 × 0.1 | 0.3 × 0.2 × 0.05 | 0.4 × 0.25 × 0.1 | 0.35 × 0.25 × 0.1 | 0.2 × 0.1 × 0.1 |
| Crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| Space group, $Z$ | $P2_12_12_1$, 4 | $P2_12_12_1$, 4 | $P2_12_12_1$, 4 | $P2_12_12_1$, 4 | $P2_12_12_1$, 4 |
| $a$ / Å | 9.5820(9) | 9.396(4) | 9.5465(6) | 9.4888(7) | 9.5605(8) |
| $b$ / Å | 14.7653(13) | 14.669(7) | 14.6856(10) | 14.7278(9) | 14.6922(11) |
| $c$ / Å | 16.1241(12) | 16.074(7) | 15.9616(12) | 15.9298(10) | 15.9600(14) |
| $\alpha$ / ° | 90 | 90 | 90 | 90 | 90 |
| $\beta$ / ° | 90 | 90 | 90 | 90 | 90 |
| $\gamma$ / ° | 90 | 90 | 90 | 90 | 90 |
| $U$ / Å$^3$ | 2281.2(3) | 2215.5(16) | 2237.8(3) | 2226.2(2) | 2241.8(3) |
| $D_{calc}$ / g cm$^{-3}$ | 1.576 | 1.625 | 1.618 | 1.626 | 1.635 |
| $\mu$(Mo Kα) / mm$^{-1}$ | 0.858 | 0.968 | 1.051 | 1.157 | 1.379 |
| $R_{int}$ | 0.0519 | 0.0383 | 0.0356 | 0.0363 | 0.0986 |
| No. reflns / params. | 5194/298 | 5052/298 | 5116/298 | 5069/299 | 5110/298 |
| $R1$ ($F^2$: $F_o^2 > 2\sigma(F_o^2)$) | 0.0295 | 0.0312 | 0.0248 | 0.0228 | 0.0462 |
| $wR2$ ($F^2$: all data) | 0.0733 | 0.0765 | 0.0613 | 0.0553 | 0.0956 |
| GoF | 1.048 | 0.992 | 1.048 | 1.058 | 1.015 |
| Flack param. | 0.003(7) | 0.032(7) | –0.009(5) | 0.001(5) | –0.005(12) |

**Table S2** Crystallographic data for compound **2A**.

| Complex | **2A** $\{[Fe(H_3L)](ClO_4)_2\}_2 \cdot H_2O$ |
|---|---|
| Chemical formula | $C_{34}H_{44}Cl_4Fe_2N_{18}O_{17}$ |
| Formula weight | 1230.37 |
| $T$ / K | 192(2) |
| Crystal color and shape | red, platelet |
| Size of specimen / mm | 0.5 × 0.4 × 0.2 |
| Crystal system | triclinic |
| Space group, $Z$ | $P\bar{1}$, 2 |
| $a$ / Å | 10.2032(3) |
| $b$ / Å | 12.8833(5) |
| $c$ / Å | 19.1031(6) |
| $\alpha$ / ° | 80.2128(17) |
| $\beta$ / ° | 79.7746(12) |
| $\gamma$ / ° | 80.6301(16) |
| $U$ / Å$^3$ | 2412.38(14) |
| $D_{calc}$ / g cm$^{-3}$ | 1.694 |
| $\mu$(Mo K$\alpha$) / mm$^{-1}$ | 0.913 |
| $R_{int}$ | 0.0303 |
| No. reflns / params. | 11031/676 |
| $R1$ ($F^2$: $F_o^2 > 2\sigma(F_o^2)$) | 0.0576 |
| $wR2$ ($F^2$: all data) | 0.1719 |
| GoF | 1.019 |

**Table S3** Comparison of structural parameters ($l$/Å, $\phi$/°) for compounds **2** and **2A**.

| Parameter[a] | **2** | **2A**(mol1) | **2A**(mol2) |
|---|---|---|---|
| M–N(a) | 1.941(3), 1.951(3), 1.935(3) | 1.934(2), 1.932(2), 1.942(2) | 1.927(3), 1.942(2), 1.955(2) |
| M–N(b) | 1.979(3), 1.974(3), 1.990(3) | 1.972(2), 1.989(2), 1.972(2) | 1.987(3), 1.986(3), 1.981(2) |
| C(a)–C(b) | 1.546(5) | 1.531(4) | 1.529(4) |
| C(b)–C(c) | 1.546(5), 1.539(5), 1.542(5) | 1.540(4), 1.532(5), 1.550(4) | 1.547(4), 1.558(4), 1.545(4) |
| N(a)–C(c) | 1.476(4), 1.460(4), 1.474(4) | 1.465(4), 1.466(4), 1.467(4) | 1.471(4), 1.467(4), 1.460(4) |
| N(a)–C(d) | 1.296(4), 1.285(5), 1.299(4) | 1.286(4), 1.281(4), 1.290(4) | 1.294(4), 1.284(4), 1.284(4) |
| C(d)–C(e) | 1.429(5), 1.424(5), 1.422(5) | 1.437(5), 1.433(4), 1.430(4) | 1.434(5), 1.439(5), 1.432(4) |
| N(b)–C(e) | 1.396(4), 1.387(5), 1.391(4) | 1.385(4), 1.395(4), 1.385(4) | 1.387(5), 1.392(4), 1.386(4) |
| C(e)–C(f) | 1.367(5), 1.362(6), 1.365(5) | 1.373(4), 1.367(4), 1.371(4) | 1.382(4), 1.361(5), 1.367(4) |
| N(b)–C(g) | 1.327(4), 1.315(4), 1.327(4) | 1.320(4), 1.315(4), 1.319(4) | 1.316(4), 1.313(4), 1.318(4) |
| N(c)–C(g) | 1.344(5), 1.349(5), 1.344(5) | 1.349(5), 1.357(4), 1.347(4) | 1.358(5), 1.342(5), 1.345(5) |
| N(c)–C(f) | 1.369(5), 1.344(6), 1.367(5) | 1.350(5), 1.355(5), 1.358(5) | 1.357(6), 1.370(5), 1.354(5) |
| N(a)–M–N(b) | 80.93(11), 81.03(13), 80.73(11) | 81.54(10), 81.00(10), 80.78(10) | 81.29(11), 81.20(11), 80.88(10) |
| N(a)–M–N(a') | 86.47(12), 86.84(11), 87.41(12) | 87.47(10), 88.12(10), 86.71(10) | 86.95(11), 86.38(10), 86.27(11) |
| N(a)–M–N(b') | 164.52(12), 163.36(12), 165.70(11)<br>100.73(12), 102.05(12), 102.60(12) | 164.14(10), 167.32(10), 164.99(10)<br>97.92(10), 100.59(10), 103.64(10) | 165.76(11), 165.02(11), 165.23(11)<br>99.96(10), 100.79(10), 100.75(11) |
| N(b)–M–N(b') | 90.64(12), 93.42(12), 92.75(12) | 89.88(10), 95.61(10), 91.59(10) | 93.15(12), 93.42(11), 93.43(11) |
| C(a)–C(b)–C(c)–N(a) | –162.4(3), –161.5(3), –162.5(3) | 161.7(3), 162.1(3), 162.1(3) | 160.2(3), 161.9(3), 159.6(3) |
| M–N(a)–C(c)–C(b) | –32.0(4), –33.5(4), –31.4(4) | 32.2(3), 31.2(3), 33.6(3) | 35.7(3), 34.9(3), 35.3(3) |
| N(b)–M–N(a)–C(c) | 165.6(2), 164.7(2), 163.2(2) | –163.5(2), –164.8(2), –162.4(2) | –165.4(2), –164.7(2), –164.5(2) |

[a] The abbreviations of atoms are:

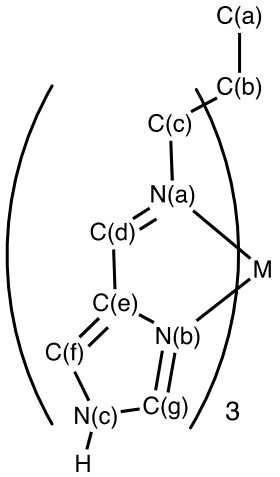


**Table S4** Hydrogen bonding parameters ($l$/Å, $\phi$/°) in compounds **1–5** and **2A**.

| D–H···A | D–H | H···A | D···A | D–H–A | symmetry code for A |
|---|---|---|---|---|---|
| Compound **1** | | | | | |
| N3–H3···Cl2 | 0.860 | 2.313 | 3.109(3) | 154.0 | –x+2, y+1/2, –z+3/2 |
| N6–H6···O1 | 0.860 | 2.184 | 2.915(4) | 142.8 | –x+2, y–1/2, –z+3/2 |
| N9–H9···Cl2 | 0.860 | 2.252 | 3.073(2) | 159.5 | x+1/2, –y+3/2, –z+1 |
| Compound **2** | | | | | |
| N3–H3···Cl2 | 0.880 | 2.249 | 3.110(3) | 165.8 | –x, y+1/2, –z+3/2 |
| N6–H6···Cl2 | 0.880 | 2.306 | 3.115(4) | 152.8 | x+1/2, –y+3/2, –z+1 |
| N9–H9···Cl2 | 0.880 | 2.424 | 3.195(4) | 146.5 | . . . |
| Compound **3** | | | | | |
| N3–H3···Cl2 | 0.880 | 2.279 | 3.121(3) | 160.0 | x–1, y, z |
| N6–H6···Cl2 | 0.880 | 2.588 | 3.249(2) | 132.6 | –x+1, y–1/2, –z+1/2 |
| N6–H6···O2 | 0.880 | 2.253 | 2.935(4) | 134.2 | –x+1, y–1/2, –z+1/2 |
| N9–H9···Cl2 | 0.880 | 2.264 | 3.090(2) | 156.2 | –x+3/2, –y+2, z–1/2 |
| Compound **4** | | | | | |
| N3–H7···Cl2 | 0.880 | 2.275 | 3.121(2) | 161.1 | . . . |
| N6–H9···Cl2 | 0.880 | 2.534 | 3.215(2) | 134.8 | –x+2, y+1/2, –z+3/2 |
| N6–H9···O4 | 0.880 | 2.308 | 2.953(3) | 130.2 | –x+2, y+1/2, –z+3/2 |
| N9–H8···Cl2 | 0.880 | 2.268 | 3.095(2) | 156.5 | –x+3/2, –y, z+1/2 |
| Compound **5** | | | | | |
| N3–H3···Cl2 | 0.880 | 2.246 | 3.080(5) | 157.9 | x–1/2, –y+1/2, –z+1 |
| N6–H6···Cl2 | 0.880 | 2.611 | 3.252(5) | 130.5 | . . . |
| N6–H6···O3 | 0.880 | 2.233 | 2.930(7) | 135.9 | –x+2, y–1/2, –z+3/2 |
| N9–H9···Cl2 | 0.880 | 2.287 | 3.122(5) | 158.4 | –x+2, y+1/2, –z+3/2 |
| Compound **2A** | | | | | |
| N3–H3···O6 | 0.880 | 2.082 | 2.910(4) | 156.4 | –x, –y+1, –z+1 |
| N6–H6···O7 | 0.880 | 2.458 | 2.940(5) | 114.9 | –x+1, –y+1, –z+1 |
| N9–H9···O14 | 0.880 | 2.374 | 3.064(5) | 135.4 | . . . |
| N12–H12···O16 | 0.880 | 2.161 | 2.894(4) | 140.4 | –x+1, –y, –z+1 |
| N15–H15···O10 | 0.880 | 2.208 | 3.041(6) | 157.9 | –x+1, –y+1, –z+1 |
| N18–H18···O17 | 0.880 | 2.130 | 2.902(5) | 146.1 | x, y, z+1 |