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# The Low Spin $Co^{II}$ Fragment with Homoleptic 1, 10-Phenanthroline Ligands: Synthesis, Structures, Magnetic Properties, and DFT Investigations

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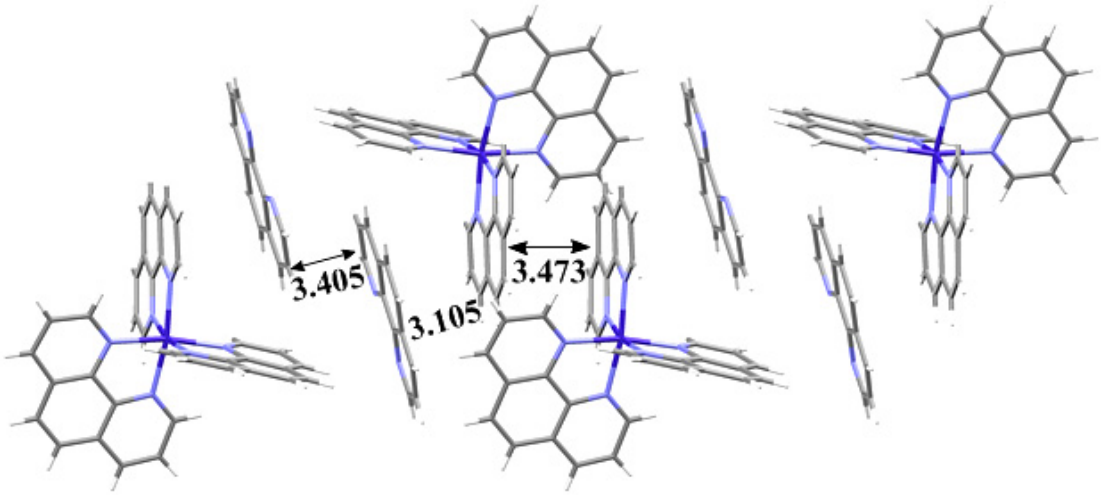


**Fig. S1.** Continuous π−π interactions between $[Co(phen)_3]^{2+}$ cations and phen molecules in crystallographic *bc* plane.

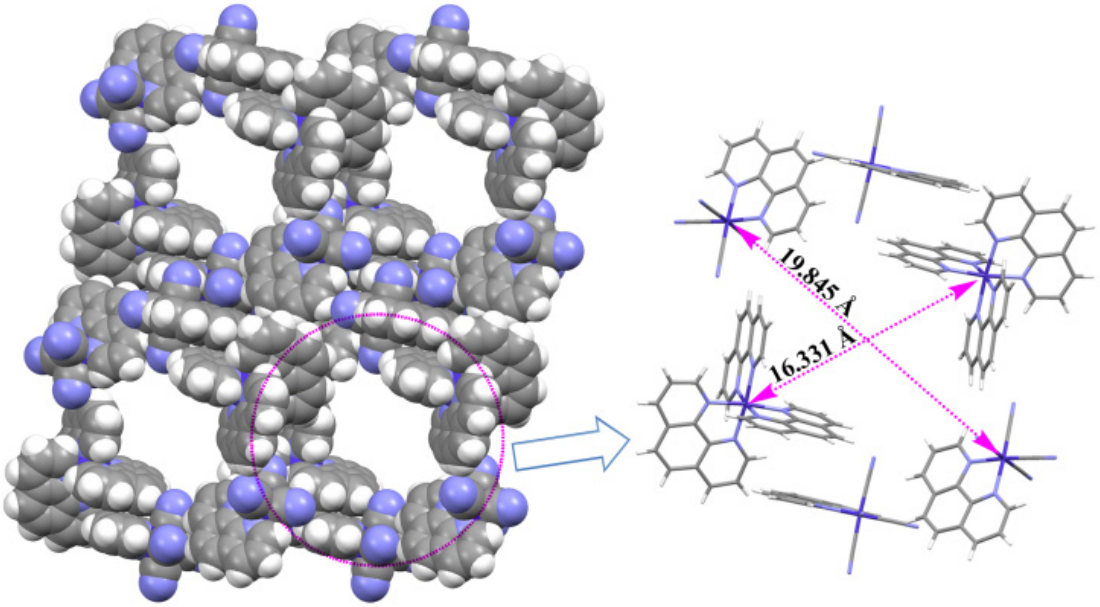


**Fig. S2.** The space-filling diagram of unoccupied cavities in the view of crystallographic *a* axis and the detail cavity structure of **1** with the diagonal distances of the void being ca. 16.331 Å and 19.845 Å.

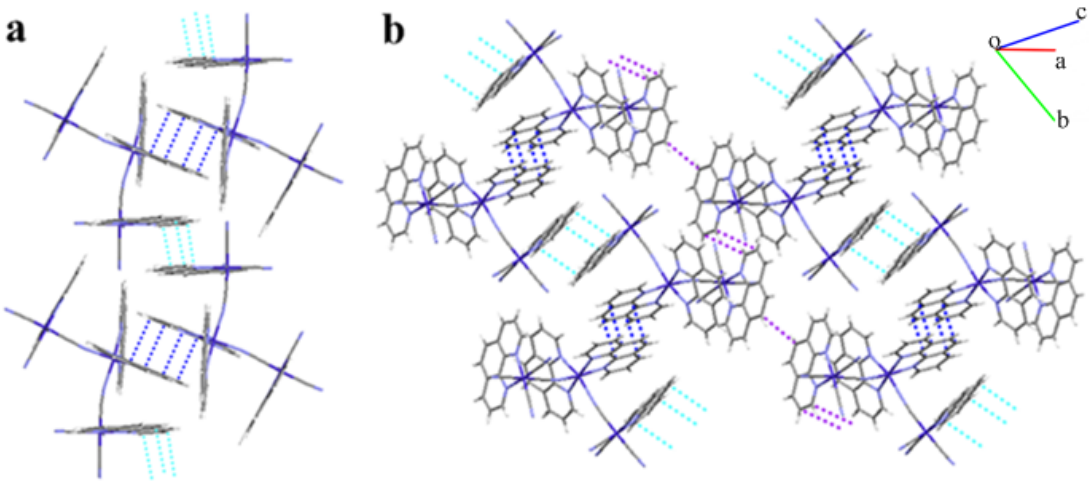


**Fig. S3.** (a) The plot of the 1D chain formed by the dimer with π−π interactions for **2**. (b) View of the 2D structure of complex **2**. (Blue dashed lines, π−π interactions within the dimer; cyano ones, π−π interactions of neighboring dimers; the purple ones, the supramolecular interactions for the formation of the 2D plane.)

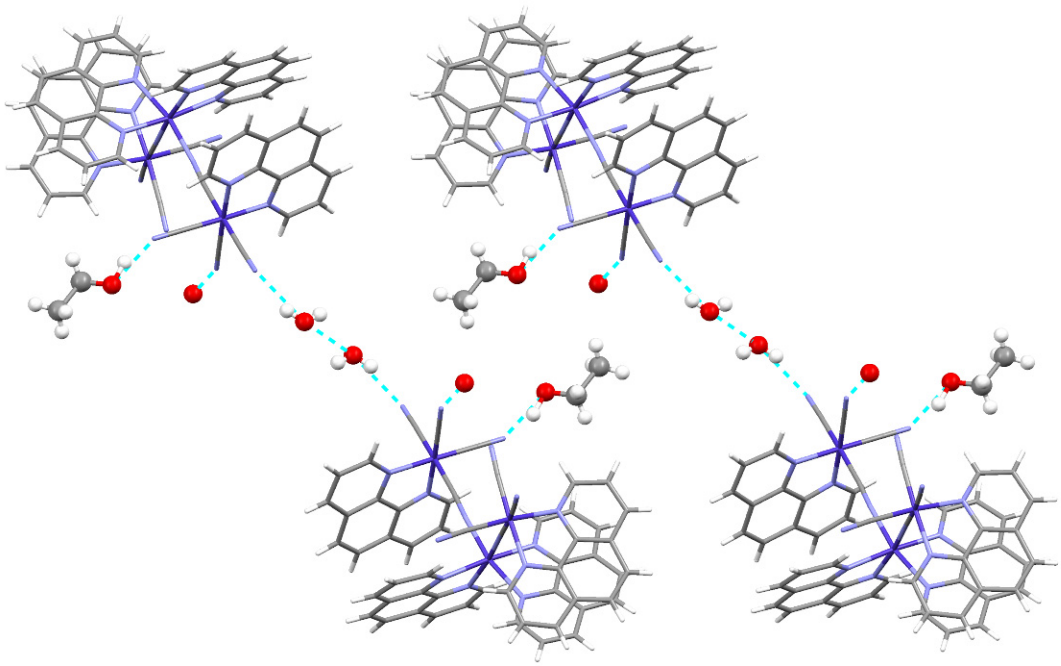

**Fig. S4.** The supramolecular structure of **2** viewed along *a* axis.

**Table S1. Selected bond distances (Å) and bond angles (°) for complex 1.**

| | | | |
|---|---|---|---|
| Co(1)-N(13) | 2.044(5) | C(2)-Co(2)-C(4) | 90.2(2) |
| Co(1)-N(11) | 2.063(5) | C(3)-Co(2)-C(4) | 88.6(2) |
| Co(1)-N(12) | 2.070(5) | C(1)-Co(2)-C(4) | 176.3(2) |
| Co(1)-N(10) | 2.074(4) | C(2)-Co(2)-N(15) | 93.7(2) |
| Co(1)-N(14) | 2.078(6) | C(3)-Co(2)-N(15) | 175.8(2) |
| Co(1)-N(9) | 2.088(4) | C(1)-Co(2)-N(15) | 91.7(2) |
| Co(2)-C(2) | 1.862(6) | N(10)-Co(1)-N(9) | 79.54(18) |
| Co(2)-C(3) | 1.867(6) | N(14)-Co(1)-N(9) | 96.41(19) |
| Co(2)-C(1) | 1.896(7) | C(2)-Co(2)-C(3) | 90.5(2) |
| Co(2)-C(4) | 1.902(6) | C(2)-Co(2)-C(1) | 87.5(2) |
| Co(2)-N(15) | 1.974(4) | C(4)-Co(2)-N(15) | 91.4(2) |
| Co(2)-N(16) | 1.977(4) | C(2)-Co(2)-N(16) | 175.8(2) |
| Co(3)-C(7) | 1.859(6) | C(3)-Co(2)-N(16) | 93.3(2) |
| Co(3)-C(5) | 1.877(6) | C(1)-Co(2)-N(16) | 91.0(2) |
| Co(3)-C(8) | 1.910(7) | C(4)-Co(2)-N(16) | 91.5(2) |
| Co(3)-C(6) | 1.931(7) | N(15)-Co(2)-N(16) | 82.49(18) |
| Co(3)-N(17) | 1.958(4) | C(7)-Co(3)-C(5) | 90.5(2) |
| Co(3)-N(18) | 1.966(4) | C(7)-Co(3)-C(8) | 89.6(2) |
| N(13)-Co(1)-N(11) | 94.7(2) | C(5)-Co(3)-C(8) | 87.5(2) |
| N(13)-Co(1)-N(12) | 97.39(18) | C(7)-Co(3)-C(6) | 87.1(2) |
| N(11)-Co(1)-N(12) | 79.3(2) | C(5)-Co(3)-C(6) | 90.6(2) |

| | | | |
|---|---|---|---|
| N(13)-Co(1)-N(10) | 168.5(2) | C(8)-Co(3)-C(6) | 176.2(3) |
| N(11)-Co(1)-N(10) | 93.32(17) | C(7)-Co(3)-N(17) | 92.9(2) |
| N(12)-Co(1)-N(10) | 92.14(18) | C(5)-Co(3)-N(17) | 176.6(2) |
| N(13)-Co(1)-N(14) | 80.2(2) | C(8)-Co(3)-N(17) | 92.6(2) |
| N(11)-Co(1)-N(14) | 169.5(2) | C(6)-Co(3)-N(17) | 89.5(2) |
| N(12)-Co(1)-N(14) | 92.1(2) | C(7)-Co(3)-N(18) | 176.2(2) |
| N(10)-Co(1)-N(14) | 93.2(2) | C(5)-Co(3)-N(18) | 93.3(2) |
| N(13)-Co(1)-N(9) | 91.85(18) | C(8)-Co(3)-N(18) | 90.7(2) |
| N(11)-Co(1)-N(9) | 92.93(18) | C(6)-Co(3)-N(18) | 92.7(2) |
| N(12)-Co(1)-N(9) | 168.37(17) | N(17)-Co(3)-N(18) | 83.26(18) |

**Table S2. Selected bond distances (Å) and bond angles (°) for complex 2.**

| | | | |
|---|---|---|---|
| Co(1)-C(2) | 1.878(4) | N(9)-Co(1)-N(10) | 83.40(11) |
| Co(1)-C(3) | 1.878(4) | N(8)-Co(2)-N(4) | 91.28(10) |
| Co(1)-C(1) | 1.900(3) | N(8)-Co(2)-N(13) | 96.22(10) |
| Co(1)-C(4) | 1.903(3) | N(4)-Co(2)-N(13) | 92.11(10) |
| Co(1)-N(9) | 1.968(3) | N(8)-Co(2)-N(12) | 168.75(10) |
| Co(1)-N(10) | 1.971(3) | N(4)-Co(2)-N(12) | 90.04(10) |
| Co(2)-N(8) | 2.080(3) | N(13)-Co(2)-N(12) | 94.89(10) |
| Co(2)-N(4) | 2.097(3) | N(8)-Co(2)-N(11) | 91.62(10) |
| Co(2)-N(13) | 2.138(3) | N(4)-Co(2)-N(11) | 89.98(10) |
| Co(2)-N(12) | 2.142(3) | N(13)-Co(2)-N(11) | 171.83(10) |
| Co(2)-N(11) | 2.158(3) | N(12)-Co(2)-N(11) | 77.21(10) |
| Co(2)-N(14) | 2.159(3) | N(8)-Co(2)-N(14) | 83.30(10) |
| Co(3)-C(7) | 1.870(3) | N(4)-Co(2)-N(14) | 167.79(10) |
| Co(3)-C(6) | 1.876(4) | N(13)-Co(2)-N(14) | 77.68(9) |
| Co(3)-C(8) | 1.894(3) | N(12)-Co(2)-N(14) | 97.41(9) |
| Co(3)-C(5) | 1.910(4) | N(11)-Co(2)-N(14) | 101.07(9) |
| Co(3)-N(15) | 1.968(2) | C(7)-Co(3)-C(6) | 91.01(14) |
| Co(3)-N(16) | 1.981(3) | C(7)-Co(3)-C(8) | 87.21(13) |
| C(2)-Co(1)-C(3) | 88.39(14) | C(6)-Co(3)-C(8) | 90.16(13) |
| C(2)-Co(1)-C(1) | 90.99(14) | C(7)-Co(3)-C(5) | 91.54(14) |
| C(3)-Co(1)-C(1) | 90.15(14) | C(6)-Co(3)-C(5) | 87.39(15) |
| C(2)-Co(1)-C(4) | 91.68(13) | C(8)-Co(3)-C(5) | 177.24(14) |
| C(3)-Co(1)-C(4) | 89.85(14) | C(7)-Co(3)-N(15) | 174.62(12) |
| C(1)-Co(1)-C(4) | 177.32(14) | C(6)-Co(3)-N(15) | 93.81(12) |
| C(2)-Co(1)-N(9) | 94.01(12) | C(8)-Co(3)-N(15) | 90.39(11) |
| C(3)-Co(1)-N(9) | 177.56(13) | C(5)-Co(3)-N(15) | 91.06(12) |
| C(1)-Co(1)-N(9) | 89.36(12) | C(7)-Co(3)-N(16) | 92.20(13) |
| C(4)-Co(1)-N(9) | 90.53(11) | C(6)-Co(3)-N(16) | 176.79(12) |
| C(2)-Co(1)-N(10) | 177.10(13) | C(8)-Co(3)-N(16) | 89.84(11) |

| | | | |
|---|---|---|---|
| C(3)-Co(1)-N(10) | 94.21(13) | C(5)-Co(3)-N(16) | 92.67(13) |
| C(1)-Co(1)-N(10) | 90.29(12) | N(15)-Co(3)-N(16) | 82.98(10) |
| C(4)-Co(1)-N(10) | 87.04(12) | | |

**Table S3. Molecular orbital energy gaps between LUMO and SOMO ($\Delta E_{\mathrm{LUMO\text{-}SOMO}}$) for the solo LS $[Co^{II}(phen)_3]^{2+}$ cation (LSC) and the one with its nearest neighbour $[Co^{III}(phen)(CN)_4]^-$ anion (LSSF) provided by different methods (in eV).**

| | **BP86** | **BPW91** | **B3LYP** |
|---|---|---|---|
| **LSC** | **0.232** | **0.244** | **2.249** |
| **LSSF** | **0.241** | **0.249** | **2.676** |