# Electronic Supplementary Information

# Enhancing the Ferromagnetic Coupling in Extended Phloroglucinol Complexes by Increasing the Metal SOMO - Ligand Overlap: Synthesis and Characterization of a Trinuclear $Co^{II}_3$ Triplesalophen Complex

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**Preparations of Compounds:** 2,4,6-Tris{[2-((5-methyl-2-hydroxyphenyl)phenylmethylimino)-phenylimino]-methyl}-1,3,5-trihydroxybenzene ($H_6$baron$^{Me}$) was synthesized as described previously.[1] The synthesis and isolation of [(baron$^{Me}$)$Co_3$] was performed using standard Schlenk line techniques under an Ar atmosphere. The Schlenk-frit with the isolated crystals was then transferred into an mBraun Glovebox. The samples for IR spectroscopy, elemental analysis, magnetic measurements, and UV-vis-NIR spectroscopy were prepared in the Glovebox.

**Computational Details:** Geometry optimization of an asymmetric Co$^{II}$ salophen complex drawn schematically in Figure S1 was performed with the program package ORCA.[2] We used the exchange potential B'88 of Becke[3] and the VWN-5 correlation potential of Vosko, Wilk, and Nusair,[4] which are described as providing a good reproduction of spin-densities.[5] The all-electron Gaussian basis sets used were those reported by the Ahlrichs group.[6] A triple-$\zeta$ valence basis set was employed with polarization functions on all atoms (def2-TZVP). Volume plots were performed with the program UCSF Chimera.[7]

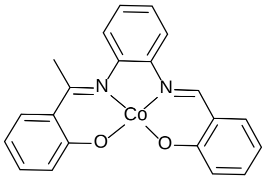

**Fig. S 1** Structure of the asymmetric Co$^{II}$ salophen complex used for the DFT calculations.

**Structure determination of [(baron$^{Me}$)$Co_3$]·DCE·$H_2O$:** $C_{71}H_{54}N_6O_7Co_3Cl_2$ ($M$ =1350.89), triclinic, space group $P\overline{1}$, $a$ = 10.2547(3) , $b$ = 16.1141(5) , $c$ = 18.9659(5) Å, $\alpha$ = 73.5170(10), $\beta$ = 89.290(2), $\gamma$ = 74.132(2)°, $V$ = 2883.48(15) Å$^3$, $Z$ = 2, $T$ = 100(2) K, $\mu$ = 8.064 mm$^{-1}$, $\rho_{calc}$= 1.556 g/cm$^3$, crystal size = 0.37 × 0.094 × 0.046 mm$^3$, 57571 reflections measured (4.87 ≤ 2$\Theta$ ≤ 133.00°), 9930 unique reflections ($R_{int}$ = 0.0467). The final $R_1$ values were 0.0420 for 8768 reflections with $I>2\sigma(I)$ and 0.0489 for all data. A single crystal of [(baron$^{Me}$)$Co_3$]·DCE·$H_2O$ was removed from the mother liquor, coated with oil and immediately cooled on a Bruker X8 PROSPECTOR ULTRA three-circle diffractometer with 4K CCD detector, Cu-K$\alpha$ radiation, Multilayer optics. CCDC 1053354 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/-data_request/cif.

The structure was solved and refined with SHELXS2013 / SHELXL2014 [8] using OLEX2.[9] During the early stages of structure completion a $C_2H_4Cl_2$ molecule was found in the asymmetric unit, which, however, suffered from strong disorder and could not be refined properly. Thus, it was removed from the coordinate set and its scattering power determined using the PLATON/SQUEEZE routine,[10] which finds approx. 40 e$^-$ per complex molecule in the solvent region. This corresponds to approx. 1 $C_2H_4Cl_2$ molecule per complex molecule, which is therefore included in the given sum formula and derived quantities.

**Table S1.** Selected interatomic distances (Å) and angles (°).

| | | | |
|---|---|---|---|
| Co1-O11 | 1.9011(17) | N22-C29 | 1.325(3) |
| Co1-O12 | 1.8340(18) | Co3-O31 | 1.8397(17) |
| Co1-N11 | 1.849(2) | Co3-O32 | 1.8221(18) |
| Co1-N12 | 1.920(2) | Co3-N31 | 1.862(2) |
| O11-C1 | 1.290(3) | Co3-N32 | 1.888(2) |
| O12-C101 | 1.312(3) | O31-C5 | 1.277(3) |
| N11-C11 | 1.314(3) | O32-C301 | 1.303(3) |
| N12-C19 | 1.328(3) | N31-C31 | 1.328(3) |
| Co2-O21 | 1.8692(18) | N32-C39 | 1.323(3) |
| Co2-O22 | 1.824(2) | C1-C2 | 1.429(3) |
| Co2-N21 | 1.840(2) | C2-C3 | 1.440(4) |
| Co2-N22 | 1.902(2) | C3-C4 | 1.405(4) |
| O21-C3 | 1.294(3) | C4-C5 | 1.448(3) |
| O22-C201 | 1.304(4) | C5-C6 | 1.422(4) |
| N21-C21 | 1.321(3) | C6-C1 | 1.458(3) |
| O11-Co1-N11 | 93.14(8) | O22-Co2-O21 | 83.85(8) |
| N11-Co1-N12 | 86.29(9) | O21-Co2-N22 | 174.25(10) |
| N12-Co1-O12 | 95.57(9) | O22-Co2-N21 | 171.64(11) |
| O12-Co1-O11 | 84.96(8) | O31-Co3-N31 | 92.62(8) |
| O11-Co1-N12 | 177.87(9) | N31-Co3-N32 | 88.24(9) |
| O12-Co1-N11 | 177.87(9) | N32-Co3-O32 | 96.13(9) |
| O21-Co2-N21 | 93.41(9) | O32-Co3-O31 | 83.00(8) |
| N21-Co2-N22 | 87.17(9) | O31-Co3-N32 | 179.12(9) |
| N22-Co2-O22 | 96.34(9) | O32-Co3-N31 | 175.56(9) |

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