# Cubane-Type $Co_4S_4$ Clusters: Synthesis, Redox Series, and Magnetic Ground States

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# Supporting Information

**Figure S-1**: (A) Temperature dependence of the effective magnetic moment, and (B) multi-field variable temperature measurement of $[Co(Pr^{i}_{2}NHCMe_2)_2(SBu^{t})_2]$ (**1**). The lines in (A) are spin Hamiltonian simulations for S = 3/2 with the following parameters: (A) $g_{Co}$ = 2.186, $D_{Co}$ = 0, and $\Theta_W$ = 0.8 K. (B): The Brillouin function for S = 3/2 calculated with $g_{Co}$ = 2., $D_{Co}$ = 0, $\Theta_W$ = 0.

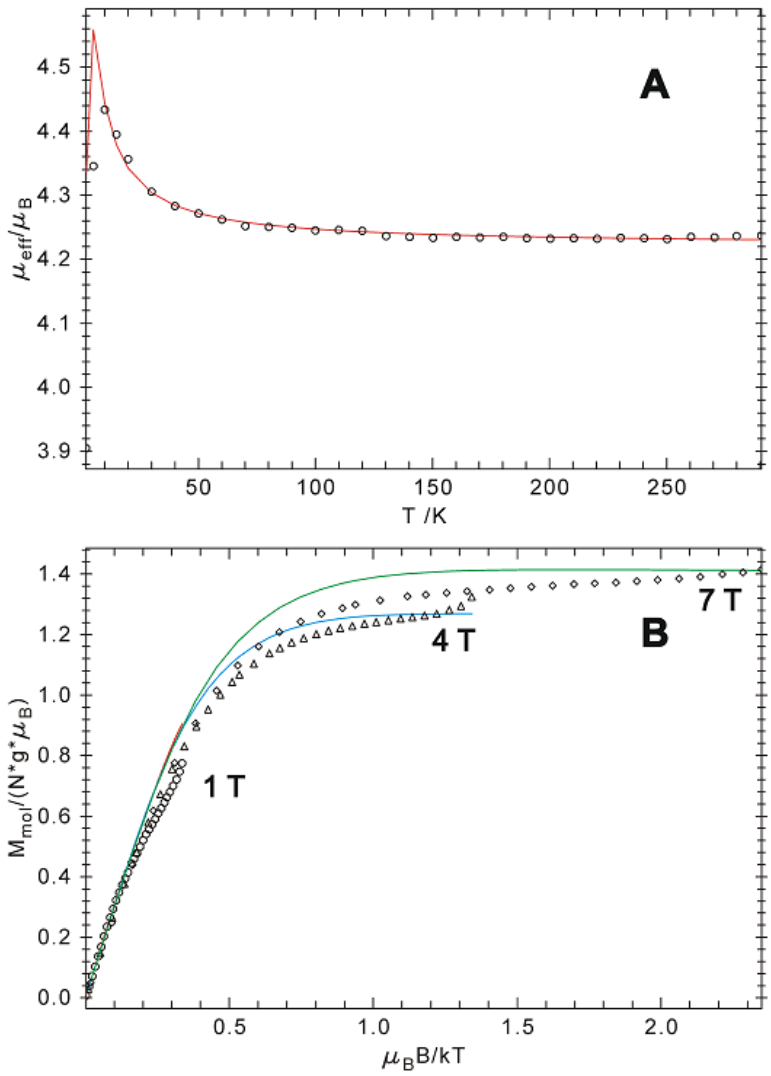
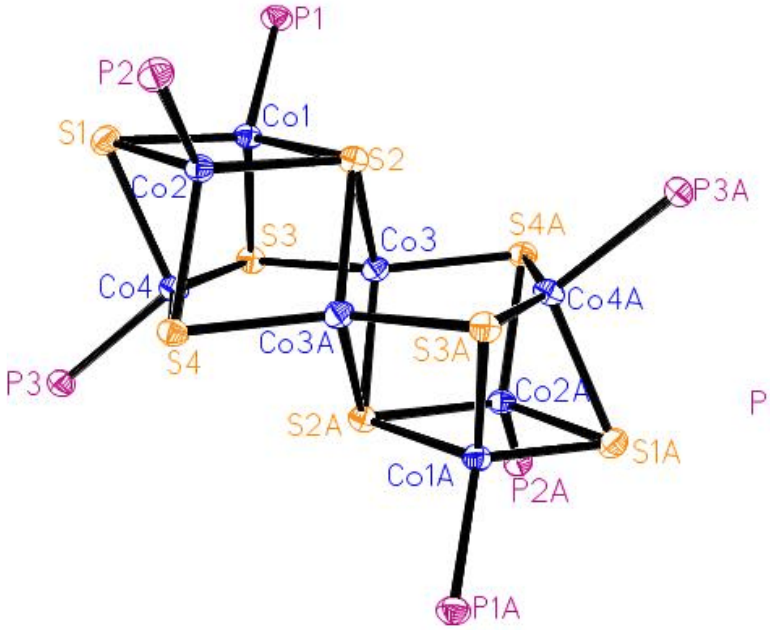



**Figure S-2**:
(A) Temperature dependence of the effective magnetic moment, and (B) multi-field variable temperature measurement of $[Co(Pr^{i}_{2}NHCMe_2)_2Cl_2]$ (**2**. The lines are spin Hamiltonian simulations for S = 3/2 with parameters for (A): $g_{Co}$ = 2.18, $D_{Co}$ = 2.3 $cm^{-1}$, and $\Theta_W$ = 0.7 K. (B): g = 2.18, $D_{Co}$ = 4.3 $cm^{-1}$, and $\Theta_W$ = 1.0 K. The values of $D_{Co}$ and $\Theta_W$ in (B) are optimized independently from those in (A).

**Figure S-3**. (A) Energies of the four total-spin manifolds for [$Co_4S_4(Pr^i_2NHCMe_2)_4$] **(5**) as function of an applied field, and calculated with the parameter used for the simulation in Figure 8 ($S_i$ = 3/2, i = 1- 4; J = -420 $cm^{-1}$, J' = -100 $cm^{-1}$, $g_1$ = 2.17, $g_{2-4}$ = 2.0, $D_i$ = 0). (B) Boltzmann population of the lowest level as function of temperature.

$[Co_8S_8(PPr^i_3)_6]^0$




$[Co_8S_8(PPr^i_3)_6]^{1+}$

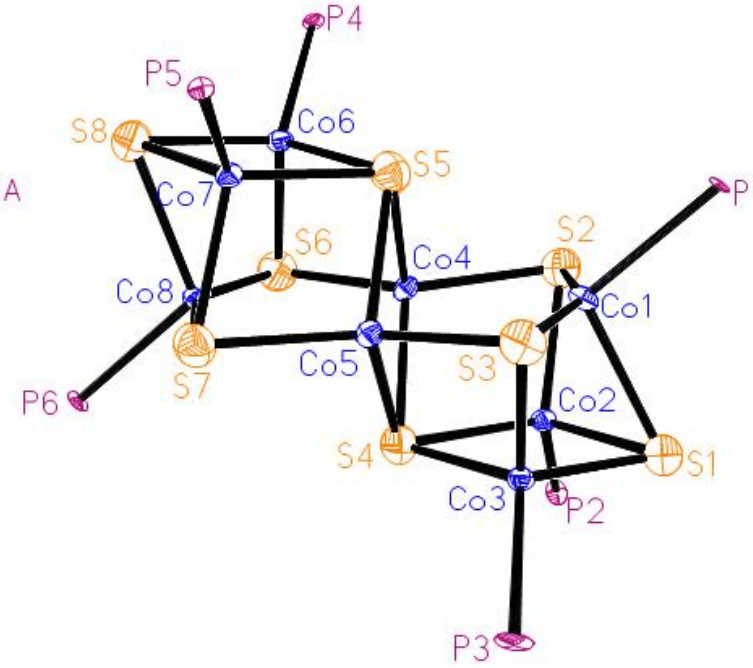


**Figure S-4**: Molecular structures of $[Co_8S_8(PPr^i_3)_6]$ (**7**) and $[Co_8S_8(PPr^i_3)_6]^{1+}$ (**8**). Isopropyl groups are omitted for clarity

**Table S-1.** Crystal Data and Summary of Data Collection and Refinement for **1**, **3**, [**4**]($BF_4$), **5**, [**6**]($BPh_4$), **7**, and [**8**]($BF_4$).[a,b]

| | **1** | **3** | [**4**]($BF_4$) | **5** | [**6**]($BPh_4$) | **7** | [**8**]($BF_4$) |
|---|---|---|---|---|---|---|---|
| formula | $C_{30}H_{58}Co$ $N_4S_2$ | $C_{36}H_{84}Co_4$ $P_4S_4$ | $C_{36}H_{84}BCo_4$ $F_4P_4S_4$ | $C_{44}H_{80}Co_4$ $N_8S_4$ | $C_{68}H_{100}B$ $Co_4N_8S_4$ | $C_{54}H_{126}Co_8P_6$ $S_8$ | $C_{54}H_{126}B$ $Co_8F_4P_6S_8$ |
| fw | 597.85 | 990.76 | 1091.68 | 1085.12 | 1404.33 | 1689.29 | 1776.10 |
| T, K | 193(2) | 130(2)) | 193(2) | 105(2) | 100(2) | 193(2) | 193(2) |
| crystal system | triclinic | monoclinic | orthorhombic | monoclinic | triclinic | triclinic | triclinic |
| space group | *P*1 | *C*2/*c* | *I*-42*m* | *Cc* | *P*-1 | *P*-1 | *P*-1 |
| *a*, Å | 9.890(1) | 19.057(3) | 12.442(1) | 14.321(3) | 9.507(1) | 12.3518(6) | 13.5596(7) |
| *b,* Å | 10.303(1) | 12.780(2) | 12.442(1) | 20.380(5) | 18.56(1) | 12.4877(6) | 20.897(1) |
| *c,* Å | 10.437(1) | 39.863(6) | 16.575(2) | 18.726(4) | 20.32(1) | 13.9495(7) | 41.467(2) |
| $\alpha$, deg | 106.082(2) | 90 | 90 | 90 | 85.581(2) | 73.960(1) | 86.085(1) |
| $\beta$, deg | 99.487(2) | 92.948(3) | 90 | 96.093(4) | 87.589(3) | 84.740(1) | 81.220(1) |
| $\gamma$, deg | 117.495(2) | 90 | 90 | 90 | 88.381(2) | 64.229(1) | 88.473(1) |
| *V*, Å$^3$ | 851.3(1) | 9695(3) | 2565.8(4) | 5434(2) | 3571(2) | 1861.2(2) | 11584(1) |
| *Z* | 1 | 8 | 2 | 4 | 2 | 1 | 6 |
| $d_{calcd}$, g/cm$^3$ | 1.166 | 1.357 | 1.413 | 1.326 | 1.306 | 1.507 | 1.528 |
| 2$\theta$ range, deg | 4.3 to 50.0 | 2.0-50.0 | 4.1-50.0 | 3.4-50.0 | 4.0-50.0 | 3.6-50.0 | 2.7-50.0 |
| GOF ($F^2$) | 0.937 | 1.070 | 1.009 | 1.027 | 1.034 | 1.027 | 1.047 |
| R1[b] | 0.0439,[d] 0.0520[e] | 0.0749,[d] 0.0919[e] | 0.0255,[d] 0.0260[e] | 0.0200,[d] 0.0205[e] | 0.0447,[d] 0.0597[e] | 0.0344,[d] 0.0393[e] | 0.0538,[d] 0.0785[e] |
| *w*R2[c] | 0.0870,[d] 0.0913[e] | 0.1981,[d] 0.2109[e] | 0.0672,[d] 0.0677[e] | 0.0489,[d] 0.0492[e] | 0.1117,[d] 0.1215[e] | 0.0893,[d] 0.0940[e] | 0.1430,[d] 0.1589[e] |

[a] Collected using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). [b] R1 = $\Sigma[(F_o - F_c)] / \Sigma(F_o)$. [c] *w*R2 = $\{\Sigma[w(F_o^2 - F_c^2)^2 / \Sigma[w(F_o^2)^2]]^{½}$. [d] I > 2_(I). [e] All data.

**Table S-2.** Selected Interatomic Distances (A) and Angles (deg) of $[Co_4S_4(PPr^i_3)_4]$ and $[Co_4S_4(Pr^i_2NHCMe_2)_4]$

**$[Co_4S_4(PPr^i_3)_4]$**

| | | | | | |
|---|---|---|---|---|---|
| Co1-S1 | 2.223(2) | Co1-Co2 | 2.618(1) | S-Co-S | 103.8(1)-106.39(7) |
| Co1-S2 | 2.229(2) | Co1-Co3 | 2.604(1) | Co-S-Co | 71.24(6)-72.00(6) |
| Co1-S3 | 2.232(2) | Co1-Co4 | 2.604(1) | | |
| Co2--S1 | 2.231(2) | Co2-Co3 | 2.602(1) | | |
| Co2-S2 | 2.236(2) | Co2-Co4 | 2.600(1) | | |
| Co2-S4 | 2.233(2) | Co3-Co4 | 2.592(2) | | |
| Co3-S2 | 2.232(2) | mean of 6 | 2.603[9] | | |
| Co3-S3 | 2.218(3) | | | | |
| Co3-S4 | 2.223(2) | Co2-P2[a] | 2.235(2) | | |
| Co4-S1 | 2.220(2) | | | | |
| Co4-S3 | 2.214(3) | P2-Co2-S1[a] | 114.6(1) | | |
| Co4-S4 | 2.210(2) | P2-Co2-S2 | 112.7(1) | | |
| mean of 12 | 2.223[8] | P2-Co2-S4 | 112.5(2) | | |

**$[Co_4S_4(Pr^i_2NHCMe_2)_4]^0$**

| | | | | | |
|---|---|---|---|---|---|
| Co1-S1 | 2.264(2) | Co1-Co2 | 2.723(1) | S-Co-S | 103.17(3)-105.26(3) |
| Co1-S2 | 2.256(1) | Co1-Co3 | 2.677(1) | Co-S-Co | 72.45(2)-74.13(3) |
| Co1-S3 | 2.240(1) | Co1-Co4 | 2.678(1) | | |
| Co2-S1 | 2.253(1) | Co2-Co3 | 2.711(1) | | |
| Co2-S2 | 2.262(1) | Co2-Co4 | 2.679(1) | | |
| Co2-S4 | 2.260(1) | Co3-Co4 | 2.680(1) | | |
| Co3-S1 | 2.250(1) | mean of 6 | 2.69[2] | | |
| Co3-S3 | 2.246(1) | | | | |
| Co3-S4 | 2.245(1) | Co1-C1 | 1.988(2) | | |
| Co4-S2 | 2.245(1) | Co2-C2 | 2.000(2) | | |
| Co4-S3 | 2.254(1) | Co3-C3 | 1.973(2) | | |
| Co4-S4 | 2.274(1) | Co4-C4 | 1.979(2) | | |
| mean of 12 | 2.25[1] | mean of 4 | 1.99[1] | | |

[a]Data for non-disordered P2 atom.

**Table S-3.** Selected Interatomic Distances (A) and Angles (deg) of $[Co_4S_4(PPr^i_3)_4]^{1+}$ and $[Co_4S_4(Pr^i_2NHCMe_2)_4]^{1+}$

**$[Co_4S_4(PPr^i_3)_4]^{1+}$**

| | | | |
|---|---|---|---|
| Co1-S1 | 2.206(1) | S1-Co1-S1A | 105.20(4) |
| Co1-S1C | 2.207(1) | S1-Co1-S1C | 104.94(3) |
| Co1-Co1A | 2.612(1) | Co1-S1-Co1C | 72.59(3) |
| Co1-Co1B | 2.606(1) | Co1-S1-Co1B | 72.44(3) |
| Co1-P1 | 2.257(1) | P1-Co1-S1 | 113.18(3) |
| | | P1-Co1-S1C | 114.49(4) |

**$[Co_4S_4(Pr^i_2NHCMe_2)_4]^{1+}$**

| | | | | | |
|---|---|---|---|---|---|
| Co1-S1 | 2.221(1) | Co1-Co2 | 2.661(1) | S-Co-S | 103.09(3)-105.69(3) |
| Co1-S2 | 2,209(1) | Co1-Co3 | 2.682(1) | Co-S-Co | 72.53(3)-74.87(3) |
| Co1-S4 | 2.223(1) | Co1-Co4 | 2.622(1) | | |
| Co2-S1 | 2.231(1) | Co2-Co3 | 2..684(1) | | |
| Co2-S2 | 2.227(1) | Co2-Co4 | 2.663(1) | | |
| Co2-S3 | 2.260(1) | Co3-Co4 | 2.658(1) | | |
| Co3-S2 | 2.204(1) | mean of 6 | 2.66[2] | | |
| Co3-S3 | 2.232(1) | | | | |
| Co3-S4 | 2.238(1) | Co1-C1 | 1.977(3) | | |
| Co4-S1 | 2.204(1) | Co2-C12 | 1.984(3) | | |
| Co4-S3 | 2.227(1) | Co3-C23 | 1.984(3) | | |
| Co4-S4 | 2.210(1) | Co4-C34 | 1.964(3) | | |
| mean of 12 | 2.22[2] | mean of 4 | 1.977[9] | | |