**SUPPLEMENTARY MATERIAL TO**

# First cobalt complexes with methyl pyruvate semi/thiosemicarbazone – synthesis, physico-chemical and structural characterization

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## ANALYTICAL AND SPECTRAL DATA FOR **1**–**4**

*[Co(Hmps)(H$_2$O)Cl$_2$] (**1**).* Yield: 52 mg (85 %). Anal. Calc. for $CoC_5H_{11}N_3O_4Cl_2$: C, 19.56; H, 3.59; N, 13.69. Found: C, 19.29; H, 3.49; N, 13.35%. Conductivity [$\Lambda_M/\Omega^{-1}$ cm$^2$ mol$^{-1}$]: 140 (in MeOH). $\mu_{eff}$ = 5.02 $\mu_B$. Selected IR bands [$\tilde{\nu}$ /cm$^{-1}$]: ν(OH, NH$_2$, NH): 3414vs, 3305s, 3231ms, 3124ms; ν(C=O): 1683vs, 1635s; ν(C=N): 1583m.

*[Co(Hmps)(H$_2$O)Br$_2$] (**2**).* Yield: 90 mg (57 %). Anal. Calc. for $CoC_5H_{11}N_3O_4,Br_2$: C, 15.17; H, 2.78; N, 10.61. Found: C, 15.08; H, 2.57; N, 10.55. Conductivity [$\Lambda_M/\Omega^{-1}$ cm$^2$ mol$^{-1}$]: 170 (in MeOH). $\mu_{eff}$ = 4.98 $\mu_B$. Selected IR bands [$\tilde{\nu}$ /cm$^{-1}$]: ν(OH, NH$_2$, NH): 3408vs, 3305vs, 3228s, 3126s; ν(C=O): 1685vs, 1634vs; ν(C=N): 1584m.

*[Co(Hmpt)$_2$][CoCl$_4$]·2H$_2$O (**3**).* Yield: 50 mg (83 %). Anal. Calc. for $Co_2C_{10}H_{22}N_6O_6S_2Cl_4$: C, 18.59; H, 3.43; N, 13.01; S, 9.92. Found: C, 18.21; H, 3.49; N, 12.87; S, 9.36%. Conductivity [$\Lambda_M/\Omega^{-1}$ cm$^2$ mol$^{-1}$]: 222 (in MeOH). $\mu_{eff}$ = 4.41 $\mu_B$ . Selected IR bands

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[$\tilde{\nu}$ /cm$^{-1}$]: ν(OH): 3400ms, ν($NH_2$, NH): 3338s, 3261s, 3150vs; ν(C=O): 1681vs; ν(C=N): 1621vs, 1605vs; ν(C=S): 958w, 855ms.

*[Co(Hmpt)$_2$]Br$_2$·Me$_2$CO (**4**)*. Yield: 68 mg (55 %). Anal. Calc. for $CoC_{13}H_{24}N_6O_5S_2Br_2$: C, 24.89; H, 3.83; N, 13.40; S, 10.22. Found: C, 24.68; H, 3.57; N, 13.55; S, 10.76%. Conductivity [$\Lambda_M/\Omega^{-1}$ cm$^2$ mol$^{-1}$]: 180 (in MeOH). $\mu_{eff}$ = 4.36 $\mu_B$. Selected IR bands [$\tilde{\nu}$ /cm$^{-1}$]: ν($NH_2$, NH): 3431ms, 3261ms, 3112s; ν(C=O): 1703m, 1672s; ν(C=N): 1624s, 1606s; ν(C=S): 958w, 857w.

Table S-I. Pertinent crystal and refinement details for **2**, **3**, and **4**.

| | **2** | **3** | **4** |
|---|---|---|---|
| Chemical formula | $C_5H_{11}Br_2CoN_3O_4$ | $C_{10}H_{22}Co_2Cl_4N_6O_6S_2$ | $C_{13}H_{24}Br_2CoN_6O_5S_2$ |
| $M_r$ | 395.92 | 646.11 | 627.23 |
| Crystal system | Monoclinic | Orthorhombic | Triclinic |
| Space group | $P2_1/c$ | $Pccn$ | $P\bar{1}$ |
| Temperature, K | 294 | 294 | 294 |
| $a$ / Å | 7.8004(2) | 14.8546(3) | 10.3796(3) |
| $b$ / Å | 13.1957(4) | 19.6095(4) | 10.9107(4) |
| $c$ / Å | 11.9046(3) | 18.0338(5) | 12.5905(5) |
| $\alpha$ / ° | 90 | 90 | 101.435(3) |
| $\beta$ / ° | 94.357(3) | 90 | 101.558(3) |
| $\gamma$ / ° | 90 | 90 | 115.576(3) |
| $V$ / Å$^3$ | 1221.82(6) | 5253.1 (2) | 1192.86(8) |
| $Z$ | 4 | 8 | 2 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ / mm$^{-1}$ | 7.94 | 1.86 | 4.28 |
| Crystal size, mm | 0.59 × 0.24 × 0.19 | 0.53 × 0.22 × 0.07 | 0.39 × 0.25 × 0.05 |
| Absorption correction | Analytical | Multi-scan | Multi-scan |
| $T_{min}$, $T_{max}$ | 0.037, 0.310 | 0.832, 1 | 0.465, 1 |
| Measured reflections | 13155 | 21982 | 18787 |
| Independent reflections | 2501 | 6243 | 5636 |
| Observed reflections [$I > 2\sigma(I)$] | 2213 | 4586 | 4619 |
| $R_{int}$ | 0.026 | 0.031 | 0.024 |
| (sin $\theta/\lambda)_{max}$ / Å$^{-1}$ | 0.626 | 0.683 | 0.685 |
| $R[F^2 > 2\sigma(F^2)]$ | 0.025 | 0.037 | 0.027 |
| $wR(F^2)$ | 0.057 | 0.092 | 0.063 |
| $S$ | 1.09 | 1.02 | 1.02 |
| Parameters | 153 | 257 | 286 |
| Restraints | 6 | 0 | 6 |
| H-atom treatment | Mixed | Constrained | Mixed |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.37, −0.40 | 0.64, −0.48 | 0.50, −0.51 |

TABLE S–II. Cremer & Pople puckering parameters for **3** and **4**

| Ring | $Q_2$ / Å | $\varphi_2$ / ° | Pucker descriptor |
|---|---|---|---|
| **3** | | | |
| Co1–S1A–C3A–N2A–N1A | 0.1979(16) | 9.2(7) | Twisted on Co1–S1A |
| Co1–S1B–C3B–N2B–N1B | 0.1230(18) | 28.2(10) | Envelope on S1B |
| **4** | | | |
| Co1–S1A–C3A–N2A–N1A | 0.3725(14) | 7.2(3) | Envelope on Co1 |
| Co1–S1B–C3B–N2B–N1B | 0.1578(15) | 19.7(7) | Twisted on Co1–S1B |

TABLE S–III. Polyhedral distortion indices for **2**–**4**

| | **2** | **3** | **4** |
|---|---|---|---|
| Average bond length / Å | 2.2766 | 2.2198 | 2.2149 |
| Polyhedral volume / Å$^3$ | 14.9428 | 13.7791 | 13.3587 |
| Distortion index | 0.07207 | 0.05141 | 0.05276 |
| Quadratic elongation / (°)$^2$ | 1.0415 | 1.0420 | 1.0591 |
| Bond angle variance | 112.4344 | 126.9278 | 175.4050 |

Distortion index, $D = \frac{1}{n}\sum_{i=1}^{n}\frac{|l_i - l_{av}|}{l_{av}}$, where $l_i$ is the distance from the central atom to the *i*th coordinating atom, and $l_{av}$ is the average bond length.

Quadratic elongation, $\langle\lambda\rangle = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{l_i}{l_0}\right)^2$, where $l_i$ is the distance from the central atom to the *i*th coordinating atom, and $l_0$ is the center-to-vertex distance of a regular polyhedron of the same volume.

Bond angle variance, $\sigma^2 = \frac{1}{m-1}\sum_{i=1}^{m}(\phi_i - \phi_0)^2$, where *m* is the number of bond angles within the polyhedron, $\phi_i$ is the *i*th bond angle, and $\phi_0$ is the ideal bond angle for a regular polyhedron (90° for an octahedron).

42 TABLE S-IV. Structural parameters (Å, °) of the complexes **3** and **4**, as well as the ligand Hmpt

| | $[Co(Hmpt)_2][CoCl_4]\cdot 2H_2O$ (**3**) | $[Co(Hmpt)_2]Br_2\cdot Me_2CO$ (**4**) | Hmpt |
|---|---|---|---|
| Co1–O1A | 2.1803(19) | 2.1472(16) | |
| Co1–O1B | 2.1878(19) | 2.1857(15) | |
| Co1–N1A | 2.092(2) | 2.1009(16) | |
| Co1–N1B | 2.077(2) | 2.0751(16) | |
| Co1–S1A | 2.3931(8) | 2.3879(7) | |
| Co1–S2B | 2.3888(8) | 2.3924(6) | |
| | | | |
| O1A–C1A | 1.217(3) | 1.227(3) | 1.208(4) |
| O1B–C1B | 1.220(3) | 1.219(3) | |
| O2A–C1A | 1.311(3) | 1.310(3) | 1.337(4) |
| O2B–C1B | 1.311(3) | 1.304(3) | |
| C1A–C2A | 1.496(4) | 1.491(3) | 1.506(6) |
| C1B–C2B | 1.487(4) | 1.499(3) | |
| N1A–C2A | 1.281(3) | 1.280(3) | 1.285(4) |
| N1B–C2B | 1.290(3) | 1.275(3) | |
| N1A–N2A | 1.354(3) | 1.350(2) | 1.367(4) |
| N1B–N2B | 1.349(3) | 1.357(2) | |
| N2A–C3A | 1.361(3) | 1.367(3) | 1.363(4) |
| N2B–C3B | 1.359(3) | 1.354(3) | |
| S1A–C3A | 1.688(3) | 1.698(2) | 1.684(4) |
| S1B–C3B | 1.698(3) | 1.703(2) | |
| N3A–C3A | 1.315(3) | 1.305(3) | 1.325(5) |
| N3B–C3B | 1.314(3) | 1.307(3) | |

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44 TABLE S-V. Hydrogen-bond geometry (Å, °) in complexes **3** and **4**

| *D*–H···*A* | *D*–H | H···*A* | *D*···*A* | *D*–H···*A* | Symmetry operation on *A* |
|---|---|---|---|---|---|
| **3** | | | | | |
| N2A–H2A···Cl1 | 0.86 | 2.47 | 3.185(2) | 141 | |
| N2B–H2B···Cl2$^{i}$ | 0.86 | 2.44 | 3.259(2) | 159 | *x*+1/2, *y*−1/2, −*z*+1 |
| N3A–H3A···Cl1 | 0.86 | 2.58 | 3.271(3) | 138 | |
| N3A–H3B···Cl3$^{ii}$ | 0.86 | 2.38 | 3.232(3) | 171 | −*x*+1, −*y*+1, −*z*+1 |
| N3B–H3D···Cl2$^{i}$ | 0.86 | 2.66 | 3.442(3) | 152 | *x*+1/2, *y*−1/2, −*z*+1 |
| N3B–H3D···O1A$^{iii}$ | 0.86 | 2.57 | 3.079(3) | 119 | −*x*+1, −*y*, −*z*+1 |
| N3B–H3C···Cl4$^{iv}$ | 0.86 | 2.39 | 3.244(3) | 176 | *x*, −*y*+1/2, *z*−1/2 |
| **4** | | | | | |
| N2A–H2A···Br1 | 0.86(2) | 2.53(2) | 3.3221(18) | 155(2) | |
| N3A–H3A···Br1 | 0.85(2) | 2.50(2) | 3.290(2) | 154(3) | |
| N3A–H3B···Br2$^{i}$ | 0.86(2) | 2.50(2) | 3.350(2) | 173(3) | −*x*+1, −*y*+1, −*z*+1 |
| N2B–H2B···Br2 | 0.84(2) | 2.46(2) | 3.2664(17) | 160(2) | |
| N3B–H3D···Br2 | 0.85(2) | 2.65(2) | 3.427(2) | 153(2) | |
| N3B–H3C···Br1$^{ii}$ | 0.85(2) | 2.56(2) | 3.405(2) | 176(2) | −*x*+1, −*y*+2, −*z*+1 |

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