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SUPPLEMENTARY MATERIAL TO

First cobalt complexes with methyl pyruvate semi/thiosemicarbazone – Synthesis, physicochemical 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. calcd. for $C_5H_{11}Cl_2CoN_3O_4$: C, 19.56; H, 3.59; N, 13.69 %. Found: C, 19.29; H, 3.49; N, 13.35 %; IR (cm^{-1}): 3414*vs*, 3305*s*, 3231*ms*, 3124*ms* (OH, NH$_2$, NH); 1683*vs*, 1635*s* (C=O); 1583*m* (C=N); Conductivity (MeOH, Λ_M / Ω^{-1} cm^2 mol^{-1}): 140. μ_{eff} (μ_B): 5.02.

*[Co(Hmps)(H$_2$O)Br$_2$] (**2**).* Yield: 90 mg (57 %); Anal. calcd. for $C5H_{11}Br_2CoN_3O_4$: C, 15.17; H, 2.78; N, 10.61 %. Found: C, 15.08; H, 2.57; N, 10.55 %; IR (cm^{-1}): 3408vs, 3305vs, 3228s, 3126s (OH, NH$_2$, NH), 1685vs, 1634vs (C=O); 1584m (C=N). Conductivity (MeOH, Λ_M / Ω^{-1} cm^2 mol^{-1}): 170; μ_{eff} (μ_B) 4.98.

*[Co(Hmpt)$_2$][CoCl$_4$]·2H$_2$O (**3**).* Yield: 50 mg (83 %); Anal. calcd. for $C_{10}H_{22}Cl_4Co_2N_6O_6S_2$: 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 %; IR (cm^{-1}): 3400*ms* (OH); 3338*s*, 3261*s*, 3150*vs* (NH$_2$, NH); 1681*vs* (C=O); 1621*vs*, 1605*vs* (C=N); 958*w*, 855*ms* (C=S); Conductivity (MeOH, Λ_M / Ω^{-1} cm^2 mol^{-1}): 222; μ_{eff} (μ_B): 4.41.

*[Co(Hmpt)$_2$]Br$_2$·Me$_2$CO (**4**).* Yield: 68 mg (55 %); Anal. calcd. for $C_{13}H_{24}Br_2CoN_6O_5S_2$: C, 24.89; H, 3.83; N, 13.40; S, 10.22 %. Found: C, 24.68;

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H, 3.57; N, 13.55; S, 10.76 %; IR (cm^{-1}]: 3431*ms*, 3261*ms*, 3112*s* (NH_2, NH); 1703*m*, 1672*s* (C=O); 1624*s*, 1606*s* (C=N); 958*w*, 857*w* ν(C=S); Conductivity (MeOH, Λ_M / Ω^{-1} cm^2 mol^{-1}): 180; μ_{eff} (μ_B): 4.36.

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

Complex	**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)
α / °	90	90	101.435(3)
β / °	94.357(3)	90	101.558(3)
γ / °	90	90	115.576(3)
V / Å^3	1221.82(6)	5253.1 (2)	1192.86(8)
Z	4	8	2
Radiation type	Mo *Kα*	Mo *Kα*	Mo *Kα*
μ / 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	φ_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**

Complex	**2**	**3**	**4**
Average bond length, Å	2.277	2.220	2.215
Polyhedral volume, Å^3	14.943	13.779	13.359
Distortion index	0.0721	0.0514	0.0528
Quadratic elongation	1.042	1.042	1.059
Bond angle variance, (°)^2	112.434	126.928	175.405

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 ith 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 ith 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, ϕ_i is the i^{th} bond angle, and ϕ_0 is the ideal bond angle for a regular polyhedron (90° for an octahedron).

TABLE S-IV. Selected bond lengths (Å) of complexes **3** and **4**, as well as the ligand Hmpt

Bond	Compound		
	$[Co(Hmpt)_2][CoCl_4]\cdot 2H_2O$ (**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)	

TABLE S-V. Hydrogen-bond geometry in complexes **3** and **4**

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