Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Organometallic sulfur complexes: reactivity studies of hydrogen sulfide anion with cobaloximes

Maria Strianese, Silvia Mirra, Valerio Bertolasi,[#] Stefano Milione, Claudio Pellecchia*

Università di Salerno, Dipartimento di Chimica, via Giovanni Paolo II, 132 I-84084 Fisciano (SA), Italy

[#] Università di Ferrara, Dipartimento di Scienze Chimiche e Farmaceutiche, Centro di Strutturistica Diffrattometrica, Via L. Borsari, 46, I - 44100 Ferrara, Italy

Contents:

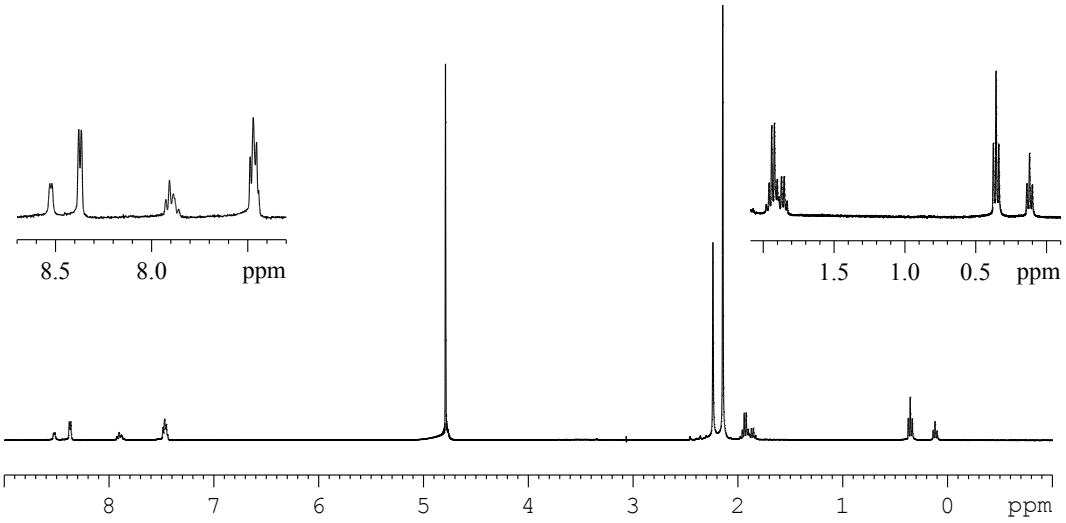


Figure S1. ^{1}H NMR spectrum of [Co(dmgH)$_2$(CH$_2$CH$_3$)(py)] (**1**) in D$_2$O (rt, 400 MHz)

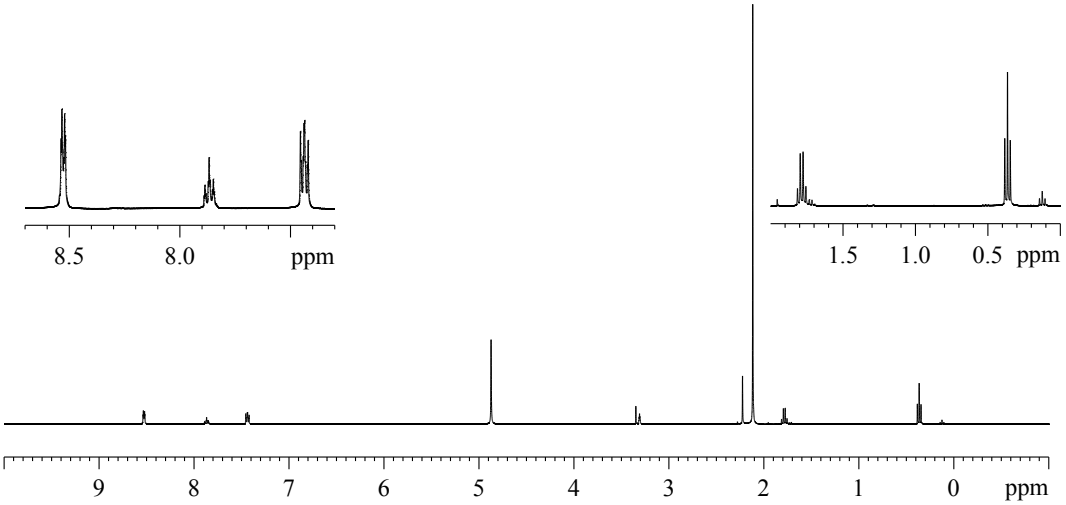


Figure S2. ^{1}H NMR spectrum of [Co(dmgH)$_2$(CH$_2$CH$_3$)(py)] (**1**)in methanol-d$_4$ (rt, 400 MHz)

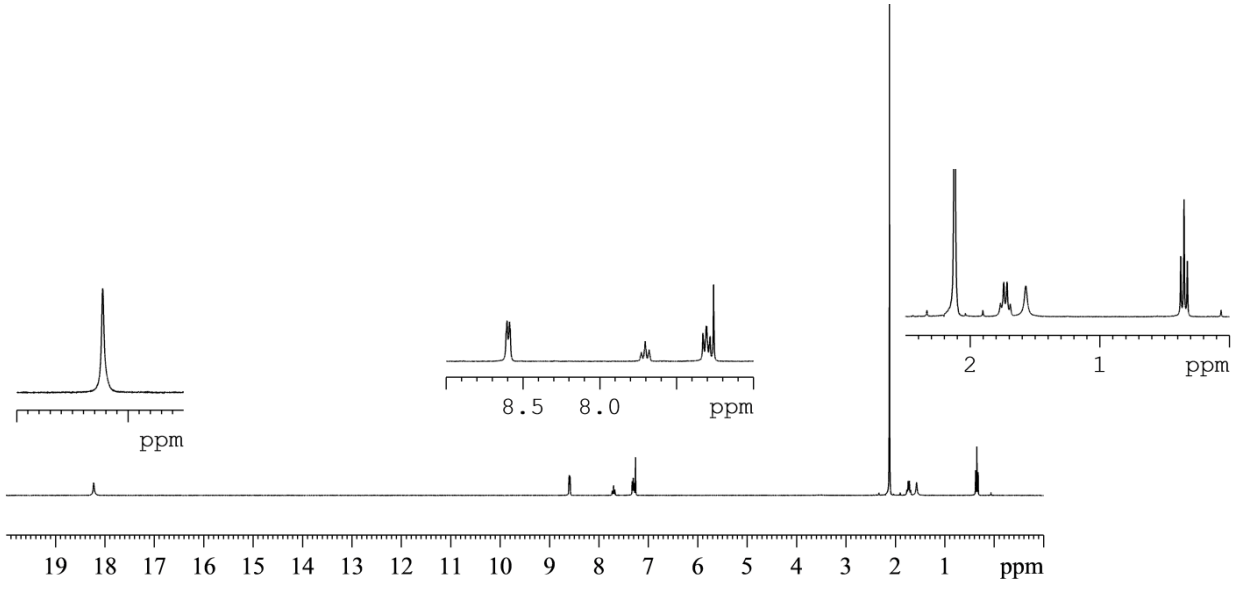


Figure S3. ^{1}H NMR spectrum of [Co(dmgH)$_2$(CH$_2$CH$_3$)(py)] (**1**) in CDCl$_3$ (rt, 400 MHz)

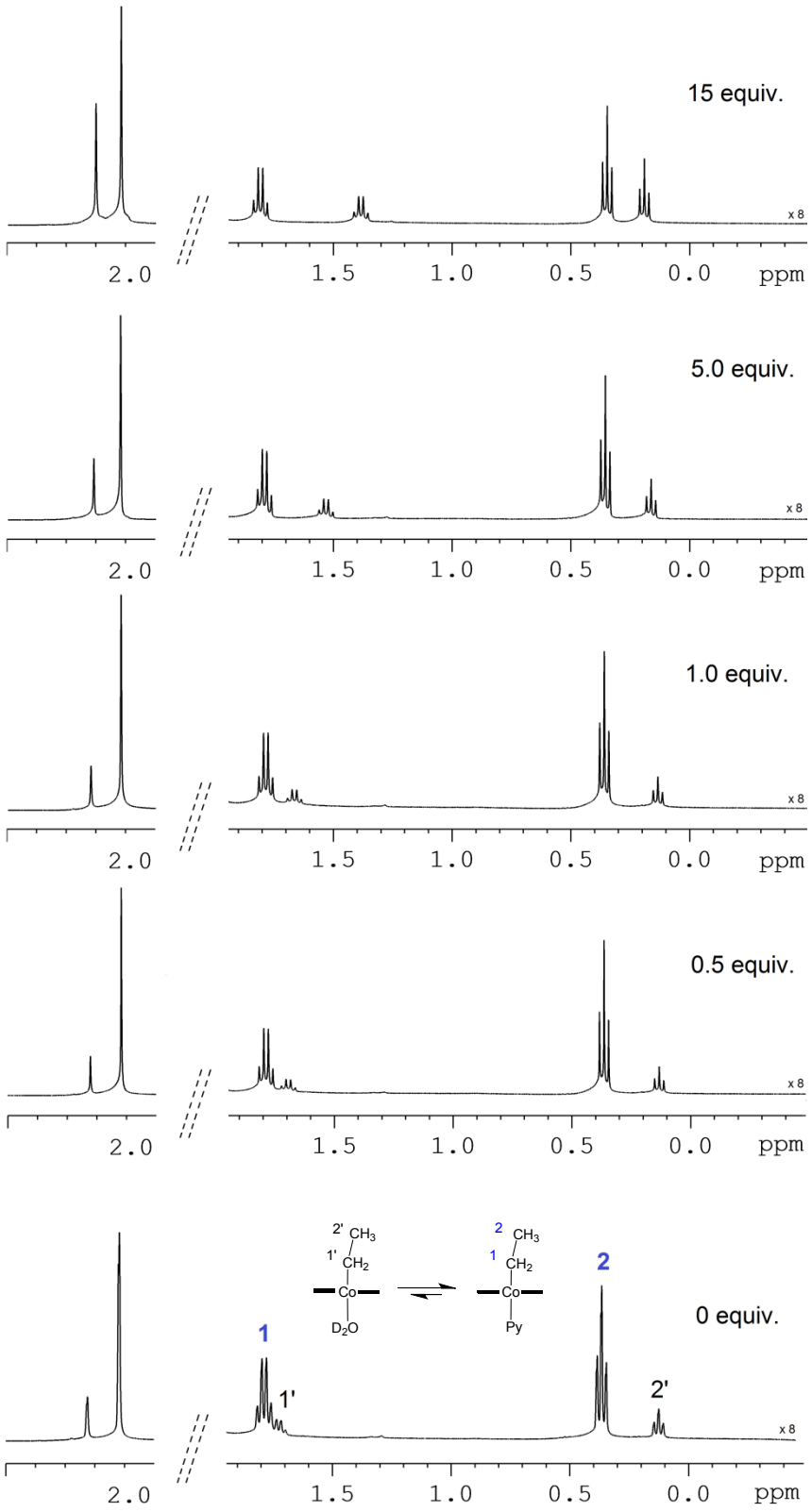


Figure S4. Aliphatic regions of the ^{1}H NMR spectrum of [Co(dmgH)$_2$(CH_2CH_3)(py)] (**1**) (dissolved in methanol-d_4) before and after the addition of 0.5, 1, 5 and 15 equivalents of KSH (dissolved in D_2O) (rt,400 MHz).

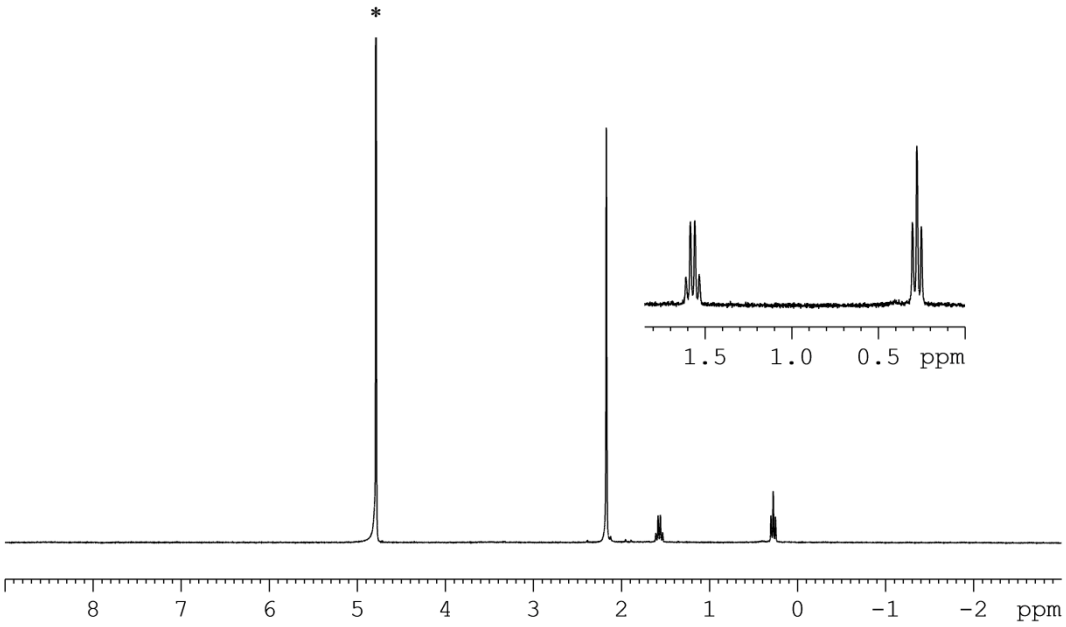


Figure S5. ^{1}H NMR spectrum of K[Co(dmgH)$_2$(CH$_2$CH$_3$)(SH)] (**2**) in D$_2$O (rt, 400 MHz)

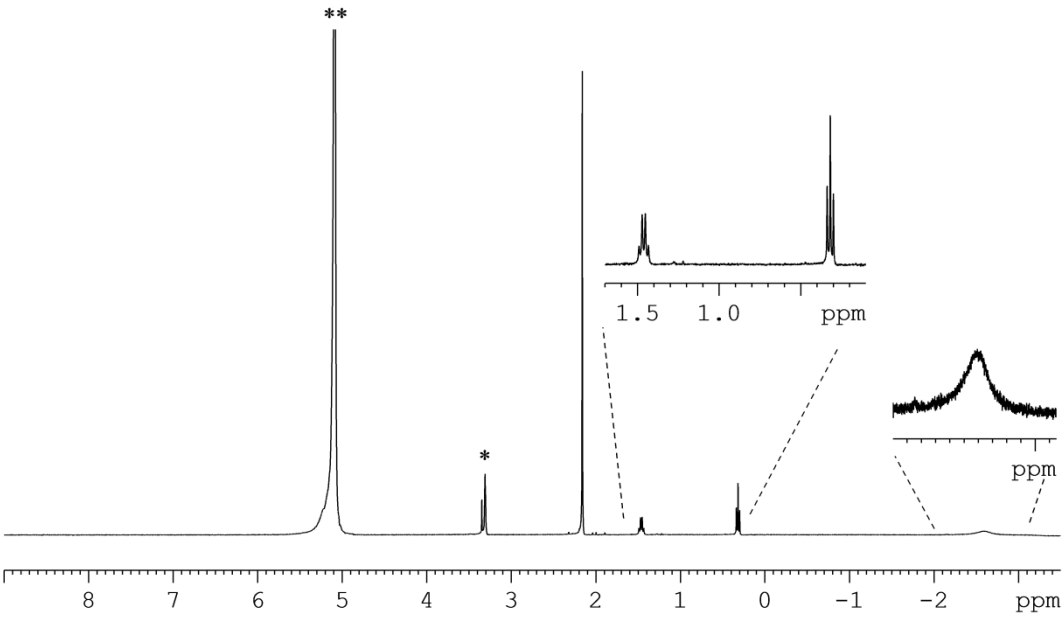


Figure S6. ^{1}H NMR spectrum of K[Co(dmgH)$_2$(CH$_2$CH$_3$)(SH)] (**2**) in methanol-d$_4$ (rt, 400 MHz)

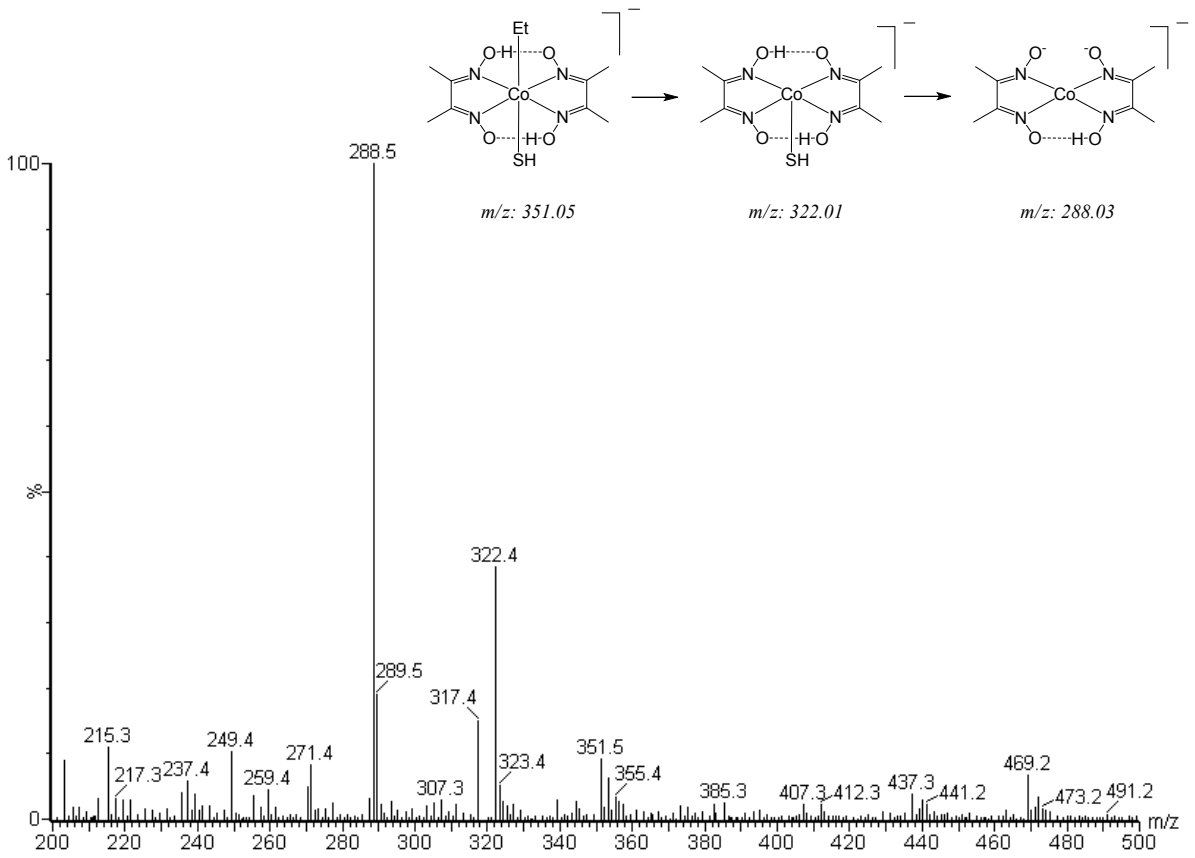


Figure S7. Electrospray mass spectra (negative-ion mode) of $K[Co(dmgH)_2(CH_2CH_3)(SH)]$ (**2**) in methanol.

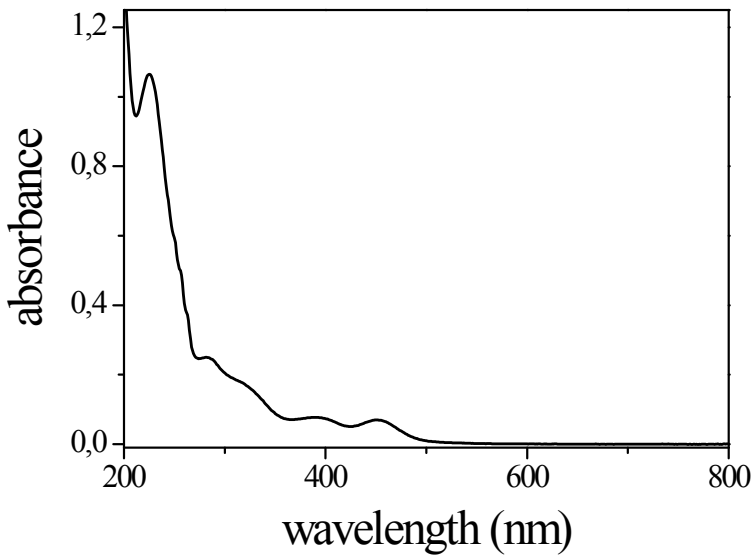


Figure S8. Electronic absorption spectra of $[Co(dmgH)_2(CH_2CH_3)(py)]$ (**1**) (rt, 3.2 x10^{-5} M, H_2O)

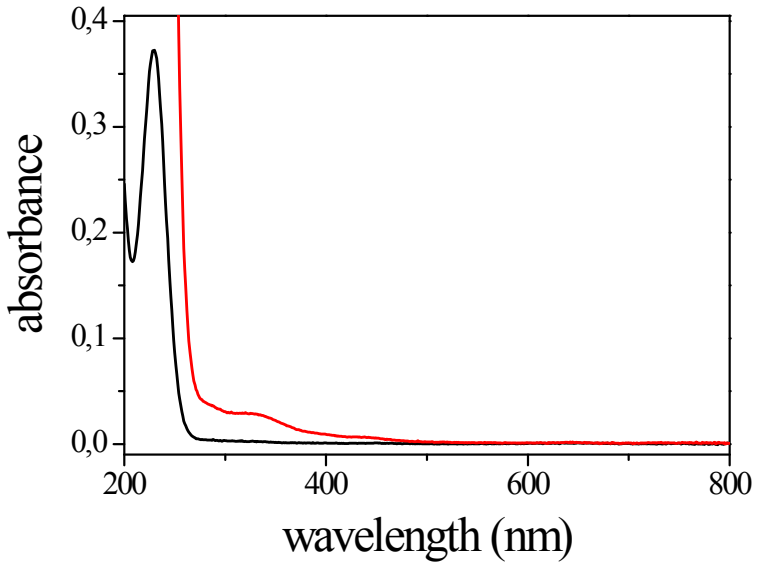


Figure S9. Electronic absorption spectra of $K[Co(dmgH)_2(CH_2CH_3)(SH)]$ (**2**) (rt, 3.2 x10^{-5} mM black line, 3.2 x10^{-4} mM red line, H_2O)

Table S1. Crystallographic data

Compound	**$K_2[Co_2(dmgH)_2(CH_2CH_3)_2(\mu\text{-}S_3)]$**
Formula	$[C_{20}H_{38}Co_2N_8O_8S_3]^{=} \bullet 2K^{+} \bullet 4H_2O$
M	882.89
Space group	*P-1*
Crystal system	Triclinic
a/Å	10.7251(2)
b/Å	11.4534(2)
c/Å	16.0740(3)
α/°	95.3842(7)
β/°	108.6656(7)
γ/°	97.8766(8)
U/Å^3	1832.95(6)
Z	2
T/K	295
D_c/g cm^{-3}	1.600
F(000)	916
μ(Mo-Kα)/cm^{-1}	13.66
Measured Reflections	27696
Unique Reflections	10526
R_{int}	0.0370
Obs. Refl.ns [I≥2σ(I)]	8614
θ_{min}- θ_{max}/°	3.30 – 30.00
hkl ranges	-15,14;-16,16;-21,22
R(F^2) (Obs.Refl.ns)	0.0355
wR(F^2) (All Refl.ns)	0.0971
No. Variables	466
Goodness of fit	1.047
$\Delta\rho_{max}$; $\Delta\rho_{min}$ /e Å^{-3}	0.743; -0.690
CCDC Deposition N.	1000024

Table S2. Selected bond distances and angles (Å and degrees) for $K_2[Co_2(dmgH)_2(CH_2CH_3)_2(\mu\text{-}S_3)]$

$[\mu\text{-}S_3\{(dmg)_2Co(Et)\}_2]K_2$			
Distances			
Co1-N1	1.859(1)	Co2-N5	1.884(2)
Co1-N2	1.874(2)	Co2-N6	1.870(2)
Co1-N3	1.879(1)	Co2-N7	1.874(2)
Co1-N4	1.880(2)	Co2-N8	1.873(2)
Co1-S1	2.3902(5)	Co2-S3	2.3757(5)
Co1-C9	2.046(2)	Co2-C19	2.052(2)
S1-S2	2.0643(6)	S2-S3	2.0475(6)
O1…O3	2.489(2)	O5…O7	2.516(3)
O2…O4	2.508(2)	O6…O8	2.474(2)
K1…S1	3.3148(7)	K2…S2	3.4018(7)
K1…S3	3.1730(7)	K2…O1	2.801(2)
K1…O2	2.806(2)	K2…O1w	2.866(2)
K1…O6	2.931(2)	K2…O2w	2.689(2)
K1…O3w	2.789(2)	K2…O3(1-x,1-y,2-z)	2.780(2)
K1…O6(-x,-y,1-z)	2.702(2)	K2…O1w(1-x,1-y,2-z)	2.751(2)
Angles			
N1-Co1-N2	82.07(7)	N5-Co2-N6	81.61(7)
N1-Co1-N3	98.84(7)	N5-Co2-N7	99.60(7)
N1-Co1-N4	179.07(7)	N5-Co2-N8	176.77(7)
N1-Co1-S1	91.09(5)	N5-Co2-S3	89.92(5)
N1-Co1-C9	89.92(7)	N5-Co2-C19	87.29(8)
N2-Co1-N3	177.84(7)	N6-Co2-N7	178.63(7)
N2-Co1-N4	98.41(7)	N6-Co2-N8	98.14(7)
N2-Co1-S1	90.95(5)	N6-Co2-S3	91.16(5)
N2-Co1-C9	89.95(8)	N6-Co2-C19	92.76(9)
N3-Co1-N4	80.64(7)	N7-Co2-N8	80.61(7)
N3-Co1-S1	90.98(5)	N7-Co2-S3	89.48(5)
N3-Co1-C9	88.09(8)	N7-Co2-C19	86.68(9)
N4-Co1-S1	89.70(5)	N8-Co2-S3	93.30(5)
N4-Co1-C9	89.29(7)	N8-Co2-C19	89.51(8)
S1-Co1-C9	178.73(6)	S3-Co2-C19	174.82(7)
Co1-S1-S2	109.63(2)	Co2-S2-S3	109.11(2)
S1-S2-S3	112.49(3)		
O3-H…O1	166(3)	O7-H…O5	171(3)
O4-H…O2	167(3)	O8-H…O6	171(4)

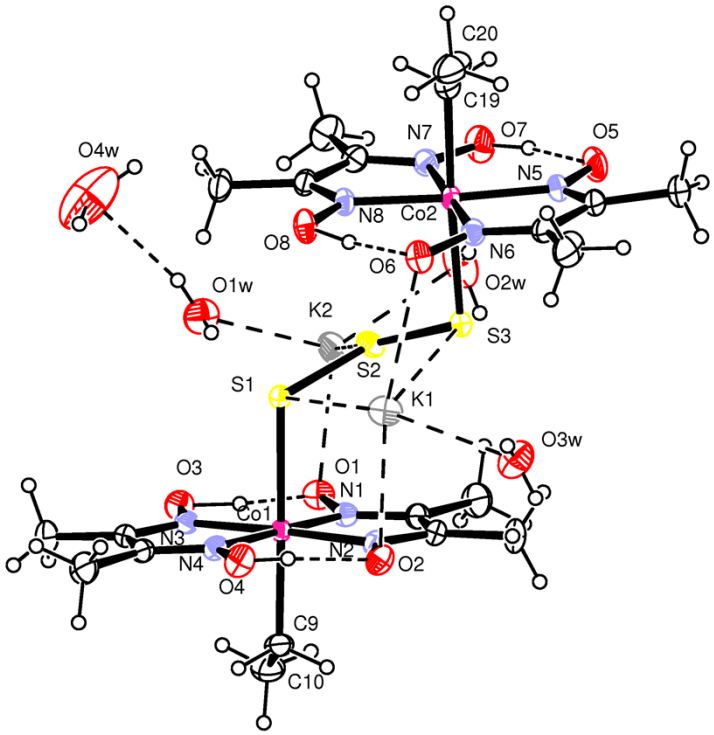
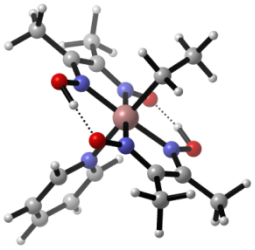


Figure S10. ORTEP view of anionic complex $K_2[Co_2(dmgH)_2(CH_2CH_3)_2(\mu\text{-}S_3)]\cdot 4H_2O$ with the thermal ellipsoids at 30% probability.

Cartesian coordinates and energies of calculated structures

[Co(dmgH)$_2$(CH$_2$CH$_3$)(py)]



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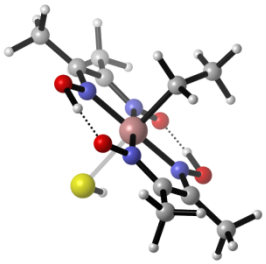
[Co(dmgH)$_2$(CH$_2$CH$_3$)(SH)]$^-$



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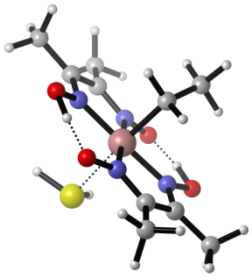
[Co(dmgH)$_2$(CH_2CH_3)(H_2S)]



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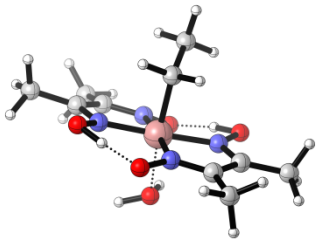
[Co(dmgH)$_2$(CH_2CH_3)(H_2O)]



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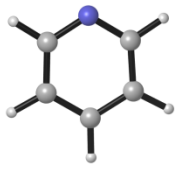
C	-3.89886700	-1.50298700	-0.04413400
H	-3.70335300	-2.45380400	-0.56619300
H	-4.19588800	-1.75508200	0.99180300
H	-4.74510500	-0.98644800	-0.52425200
C	0.47328400	-1.03189800	2.66290700
H	-0.01915000	-1.97066000	2.35489300
H	1.55956400	-1.15227400	2.50863200
H	0.30782900	-0.91590600	3.75438000

E = -2371.62811861 a.u.
G = -2371.64120687 a.u.
E(H_2O) = -2371.364008 a.u.
G(H_2O) = -2371.377096 a.u.

Pyridine

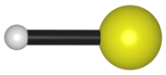


Charge = 0
Multiplicity = 1

C	-3.550078	-1.224570	0.000030
C	-2.145571	-1.230836	-0.000067
C	-1.473096	0.000074	-0.000270
C	-2.233468	1.178705	-0.000402
C	-3.633784	1.070102	-0.000323
N	-4.299594	-0.103053	-0.000085
H	-0.377824	0.040012	-0.000359
H	-4.108106	-2.170912	0.000184
H	-1.596174	-2.178520	0.000037
H	-1.754619	2.163921	-0.000554
H	-4.259290	1.973259	-0.000379

E = -248.28027283 a.u.
G = -248.221476 a.u.
E(H_2O)= -248.28505789 a.u.
G(H_2O) = -248,22626106 a.u.

HS^-

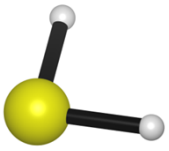


Charge = -1
Multiplicity = 1

S	0.000000	0.000000	0.080753
H	0.000000	0.000000	-1.292049

E = -398.83041162 a.u.
G = -398.842571 a.u.
E(H_2O) = -398.94551057 a.u.
G(H_2O) = -398,95766995 a.u.

H_2S

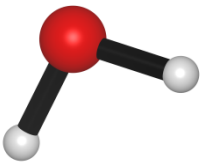


Charge = 0
Multiplicity = 1

S	0.000000	0.000000	0.104757
H	0.000000	0.980167	-0.838057
H	0.000000	-0.980167	-0.838057

E = -399.40827076 a.u.
G = - 399.413118 a.u.
E(H_2O)= -399.41236246 a.u.
G(H_2O) = -399,41720970 a.u.

H_2O



Charge = 0
Multiplicity = 1

O	0.509291	-0.181246	0.000000
H	1.485301	-0.125690	0.000000
H	0.235862	0.757326	0.000000

E = -76.40919764 a.u.
G = -76.41646378 a.u.
E(H_2O)= -76.406309 a.u.
G(H_2O) = -76.413575 a.u.