

Electronic Supplementary Information

Synthesis and crystal structure of a rare square-planar Co (II) complex of a hydroxyamidinate ligand.

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1) Materials and Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ at room temperature (r.t.) on the following spectrometers: Bruker AV-400, AV-300, DRX-400, and ARX-300 MHz. Chemical shifts (δ) are reported in part per million (ppm) relative to TMS, using the residual solvent protons (7.26 ppm) as reference. Absorption spectra were measured in DCM at r.t. on a Cary 500i UV-Vis-NIR Spectrophotometer. Electrochemical measurements were carried out in argon-purged dry DCM at room temperature with a BAS CV50W multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 475 mV vs SCE in DCM. The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates of 50, 100, 200, and 500 mV/s. For irreversible oxidation processes, the cathodic peak was used as E. Accurate mass measurements were performed on a LC-MSD-Tof instrument from Agilent Technologies in positive electrospray. For the ligand, aliquots of 0.1 uL were injected into the mass spectrometer using a 0.5 mL/min flow of 75% methanol/ 25% water mixture. The capillary voltage was set at 3000 V and mass spectra were acquired from 100 to 3000 m/z. Protonated molecular ions [M+H]⁺ were used for empirical formula confirmation. For the complex, the sample was infused into the mass spectrometer at a flow rate of 20 uL/min, the capillary voltage was set at 3500 V, and mass spectra were acquired from 105 to 3200 m/z. Both the molecular ion [M]⁺ and the sodium adduct [M+Na]⁺ were used for empirical formula confirmation. The microanalyses were done by the Elemental Analysis Service at

Université de Montréal. Solvents, purchased from VRW and Fisher, were removed under reduced pressure using a rotary evaporator, unless otherwise stated. The *m*-CPBA from Acros Organics and the aniline, triethylorthoformate, and metal salt from Aldrich, were used without further purification.

2) Experimental procedure

***N*-Hydroxy-*N,N'*-bis(2,6-dimethyl)formamidine (2):** A solution of *m*-CPBA (0.89 g, 4.0 mmol, 1 eq.) in DCM (20 mL) was added drop-wise by addition funnel to a solution of compound **1** (1.0 g, 4.0 mmol, 1 eq.) in DCM (20 mL) at 0 °C (ice bath). The reaction mixture was allowed to warm to room temperature and was stirred for other 30 minutes and then was washed with an aqueous solution of K₂CO₃ (5%) (2 x 25 mL). The combined organic fractions were dried over anhydrous MgSO₄ and filtered. The solvent was removed by evaporation to afford a solid that was further purified by recrystallization in DCM/ hexane (1:1) at -10 °C. A colorless solid was obtained and was dried under vacuum overnight.

Yield: 0.98 g, 92%. ¹H-NMR (CDCl₃, 400 MHz) δ 7.34 (s, 1H, -NH-**CH**=N-), 7.20 (t, J^t = 8 Hz 1H, -C₆**H**₃), 7.15-7.06 (m, 5H, -C₆**H**₃), 3.51 (bs, OH), 2.38 (d, J^d = 3 Hz, 12H, **CH**₃). ¹³C {¹H} NMR (CDCl₃, 75 MHz) δ, ppm: 142.1, 140.4, 135.8, 134.8 (2C), 133.4, 129.3, 129.0 (2C), 128.6 (2C), 126.7, 18.81 (2C), 17.26 (2C). Elemental Analysis: *calc.* (%) for C₁₇H₂₀N₂O·0.5CH₂Cl₂: C 67.62, H 6.81, N 9.01; *found*: C 68.19, H 6.81, N 9.00. MS (ESI - DCM) (m/z): 269.2 [M+H]⁺ (100%).

Bis(*N*-hydroxy-*N,N'*-Bis(2,6-dimethylphenyl)formamidinate)cobalt(II) (3): A solution of the ligand **2** (0.10 g, 0.37 mmol, 2 eq.) in aq. EtOH 90% was slowly added to a solution of metal salt Co(OAc)₂·4H₂O (0.046 g, 0.19 mmol, 1 eq.) in water. The formation of a green precipitate is observed almost instantly. After stirring for 90 min. at r.t., water was added and the reaction mixture was kept at 4°C for 2 h, before being filtered. The resulted solid was washed with hot water and aq. EtOH 50%, and was taken in DCM and dried over Mg₂SO₄. A second filtration and solvent evaporation yielded the desired product as a green powder. X-ray quality crystals obtained by slow diffusion of hexane in DCM at -10 °C.

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Yield: 0.090 g, 81%. ^1H NMR paramagnetic compound Co (II) d^7 : (CDCl_3 , 300 MHz) δ , ppm: 47.39; 36.92; 23.20; 7.28; -0.31; -5.62; -45.38; -50.84. IR (ATR, solid sample, cm^{-1}) 3008, 2968, 2947, 2913, 2851, 1601, 1578, 1466, 1269, 1227, 1202, 1092, 987, 928, 918, 892, 821, 777, 755, 741, 694, 639, 527, 497, 488. Elemental Analysis: calc. (%) for $\text{C}_{34}\text{H}_{38}\text{CoN}_4\text{O}_2$: C 68.79, H 6.45, N 9.44; found: C 68.52, H 6.42, N 9.27. MS (ESI-HRMS DCM – no acid) (m/z): $[\text{M}]^+$ $\text{C}_{34}\text{H}_{38}\text{CoN}_4\text{O}_2$: calc. 593.2321; found 593.2305. $[\text{M}+\text{Na}]^+$ $\text{C}_{34}\text{H}_{38}\text{CoN}_4\text{NaO}_2$: calc. 616.2219; found 616.2212. UV-vis: (DCM, 5×10^{-4} M) $[\lambda, \text{nm} (\epsilon, \text{M}^{-1}\text{cm}^{-1})]$: 540 (79), 622 (12), 942 (29), 1233 (27). E-chem (values vs. SHE) (in 0.1 M TBAPF₆ in DCM; scan rate is 100 mV s^{-1}) $\text{Co}^{2+/3+}$, +0.47 V (r); ligand, +1.70 V (irr); no reduction observed.

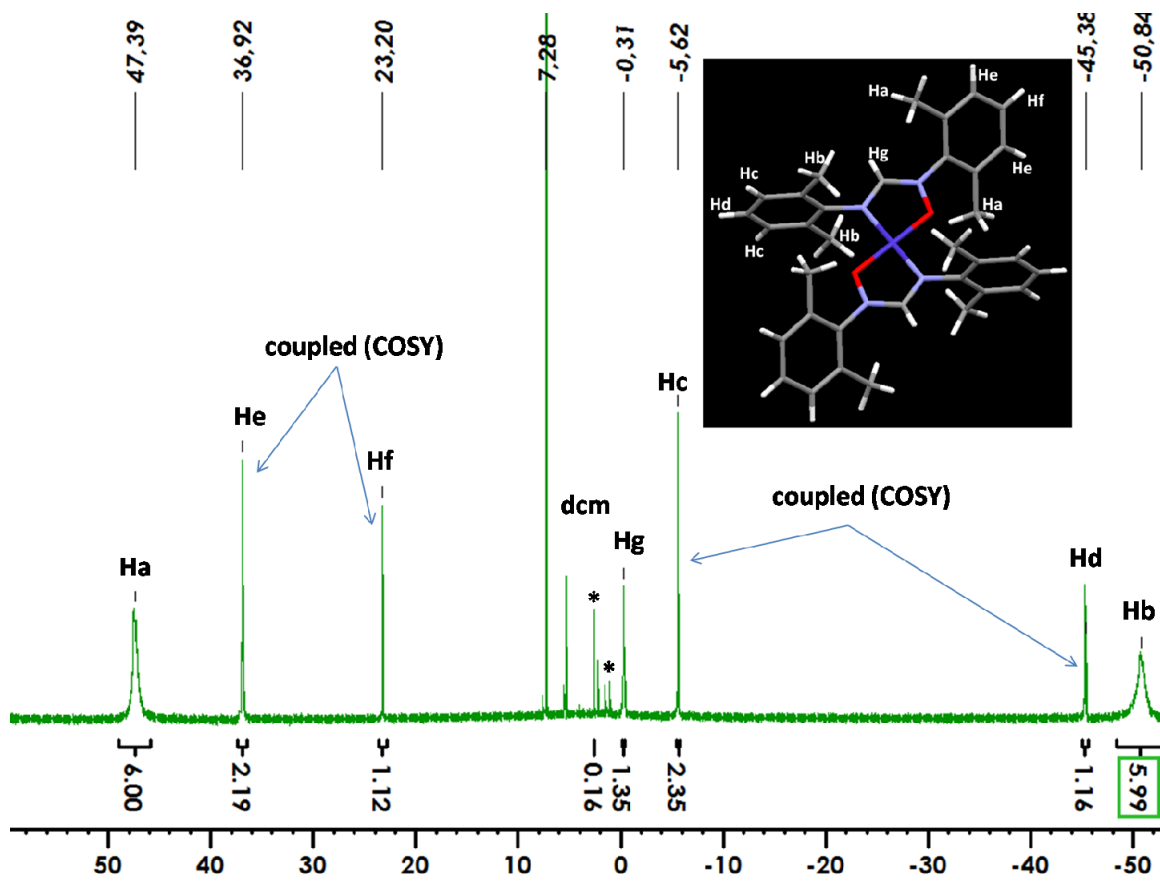


Figure S1: The $^1\text{H-NMR}$ of **3** in CDCl_3 showing a characteristically expanded paramagnetic spectrum (50 to -50 ppm) in line with the oxidation state of the metal (Co^{II} , d^7) and the tentative assignment of the signals (impurities and/or solvents are marked with an asterisk).

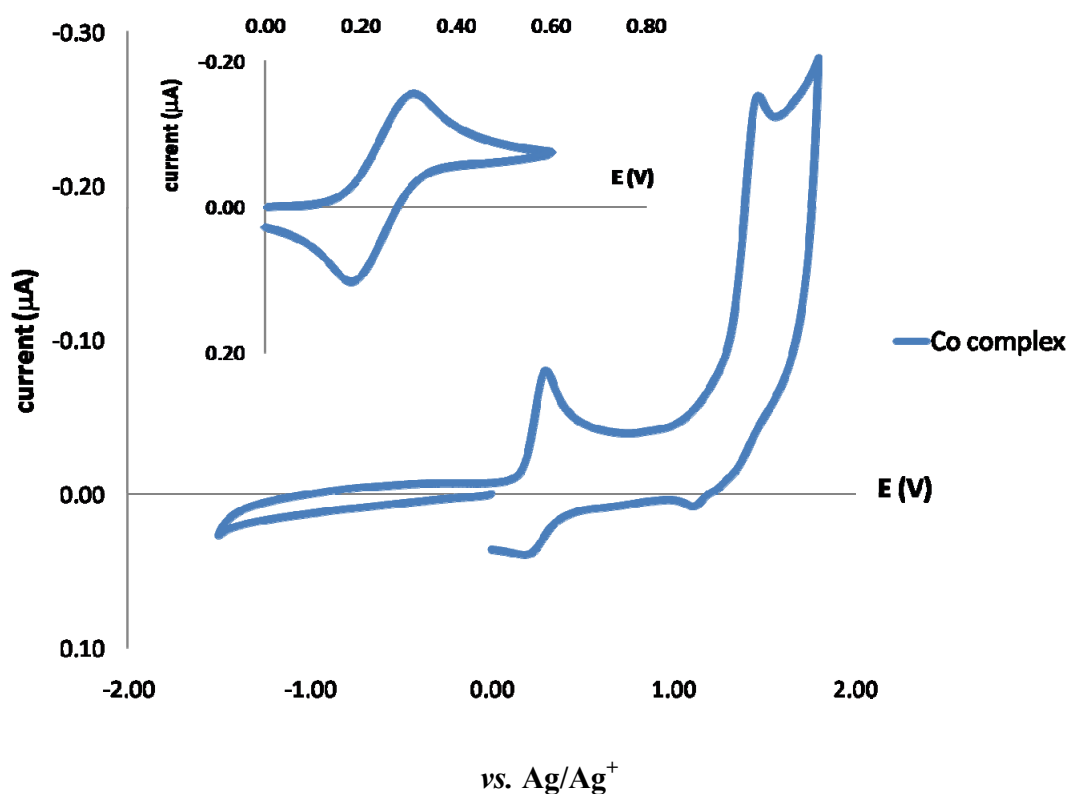


Figure S2 The CV of **3** showing the reversible oxidation of metal (+0.47 V vs. SCE) and the irreversible oxidation of the ligand (+1.70 V vs. SCE) (the plot is vs. Ag/Ag^+); conditions: 0.1 M TBAPF_6 in DCM, scan rate 100 mV s^{-1} , $[\text{complex}] = 1 \text{ mM}$.

Table 1. Selected geometric parameters for compound 3 (in Å and °)

Co1-O1	1.8341(9)	O1-Co1-N2	84.5(1)
Co1-N2	1.8856(11)	N1-O1-Co1	111.5(1)
N1-O1	1.392(2)	N1-Co1-N2	116.8(3)
C1-N1	1.319(2)	C1-N1-O1	115.1(2)
C1-N2	1.312(2)	N2-Co1-O1-N1	179.0(1)
N1-C11	1.428(2)	Co1-N2-C1-N1	1.3(2)

N2-C21	1.430(2)	Co1-O1-N1-C11	177.0(1)
C15-C16	1.395(2)	O1-Co1-N2-C21	178.5(2)

Table 2. Crystal data and structure refinement for compound 3

Empirical formula	C34 H38 Co N4 O2
Formula weight	593.61
Temperature	200K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 8.8879(12) Å $\alpha = 90^\circ$ b = 8.3485(11) Å $\beta = 93.057(2)^\circ$ c = 20.363(3) Å $\gamma = 90^\circ$
Volume	1508.8(3) Å ³
Z	2
Density (calculated)	1.307 g/cm ³
Absorption coefficient	0.606 mm ⁻¹
F(000)	626
Crystal size	0.24 x 0.18 x 0.16 mm
Theta range for data collection	2.00 to 31.35°
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -28 ≤ l ≤ 29
Reflections collected	36660
Independent reflections	4749 [Rint = 0.041]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9076 and 0.5647
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4749 / 0 / 191
Goodness-of-fit on F ²	0.975
Final R indices [I > 2σ(I)]	R ₁ = 0.0367, wR ₂ = 0.1008
Largest diff. peak and hole	

R indices (all data)	$R_1 = 0.0512$, $wR_2 = 0.1066$
Largest diff. peak and hole	0.858 and $-0.336 \text{ e}/\text{\AA}^3$

Table 3. Crystal data and structure refinement for compound 4

Empirical formula	C ₃₄ H ₃₈ Co N ₄ O ₂
Formula weight	593.61
Temperature	200K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 8.8879(12) \text{ \AA}$ $\alpha = 90^\circ$ $b = 8.3485(11) \text{ \AA}$ $\beta = 93.057(2)^\circ$ $c = 20.363(3) \text{ \AA}$ $\gamma = 90^\circ$
Volume	1508.8(3) Å ³
Z	2
Density (calculated)	1.307 g/cm ³
Absorption coefficient	0.606 mm ⁻¹
F(000)	626
Crystal size	0.24 x 0.18 x 0.16 mm
Theta range for data collection	2.00 to 31.35°
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-28 \leq l \leq 29$
Reflections collected	36660
Independent reflections	4749 [Rint = 0.041]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9076 and 0.5647
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4749 / 0 / 191
Goodness-of-fit on F ²	0.975
Final R indices [I > 2σ(I)]	$R_1 = 0.0367$, $wR_2 = 0.1008$

Largest diff. peak and hole	$R_1 = 0.0512$, $wR_2 = 0.1066$
R indices (all data)	0.858 and $-0.336 \text{ e}/\text{\AA}^3$
Largest diff. peak and hole	

Table 4. Selected geometric parameters for compound 4 (in Å and °)

Co1-O1	1.954(2)	N1-C11	1.425(4)
Co1-N2	2.126(2)	N2-C21	1.426(4)
Co1-N5	2.090(4)	O1-Co1-N2	97.21(9)
N1-O1	1.383(3)	N1-O1-Co1	112.32(17)
C1-N1	1.321(4)	O1-Co1-N5	110.20(8)
C1-N2	1.296(4)	C1-N1-O1	118.0(3)
