

Supporting Information

Controlling oxidation of bis-tridentate cobalt(II) complexes having bis(2-pyridylalkyl)amines: Ligand vs. metal oxidation

S. Anjana,^{*a} S. Donring,^b P. Sanjib,^c B. Varghese^d and Narasimha N. Murthy^a

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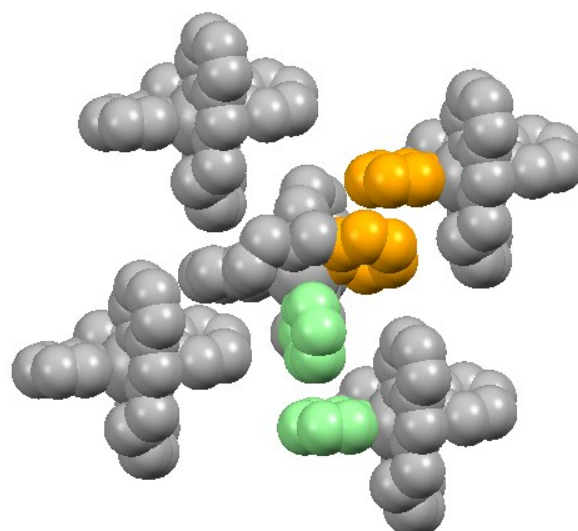


Figure S1. Part of a sheet of $[\text{Co}(\text{pepmi})_2]^{2+}$ cations in **2** showing “tpy embrace”. H- atoms and counter anions are omitted for clarity

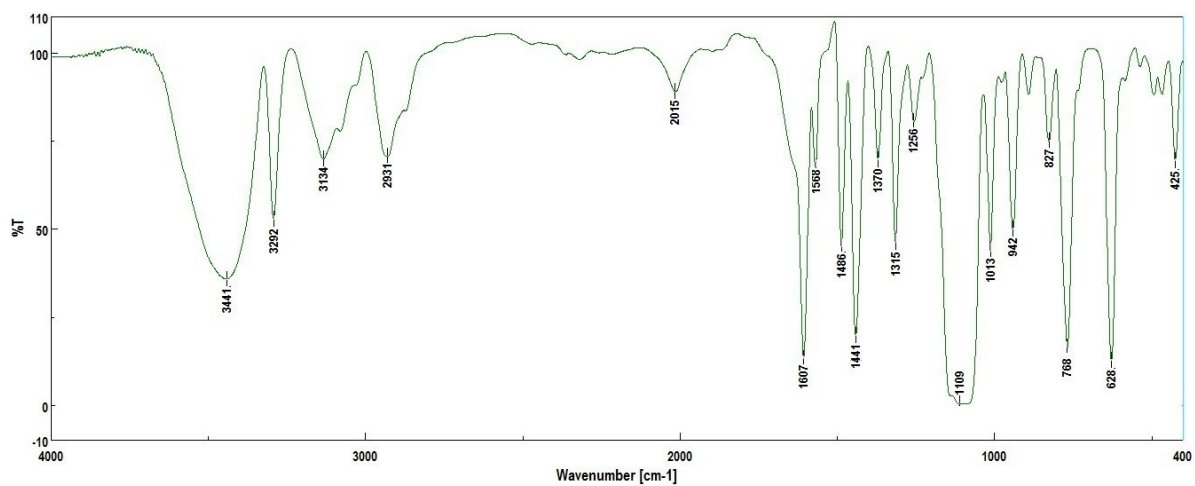


Figure S2. FT-IR of Co(II) amine complex **1** (characteristic -NH stretch is seen at 3292 cm^{-1})

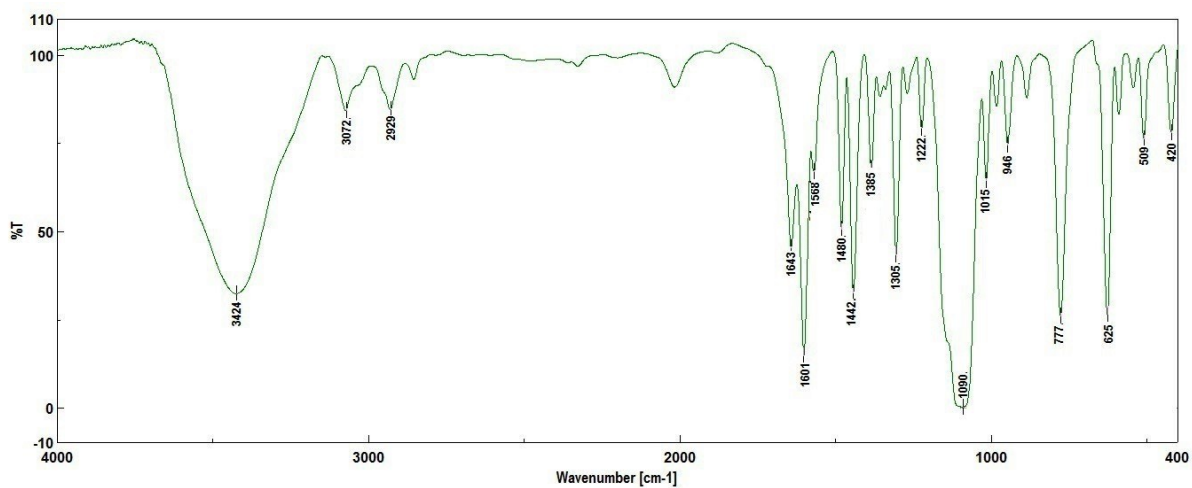


Figure S3. FT-IR of Co(II) imine complex **2** (-NH stretch is absent and characteristic -C=N stretch is seen at 1643 cm^{-1})

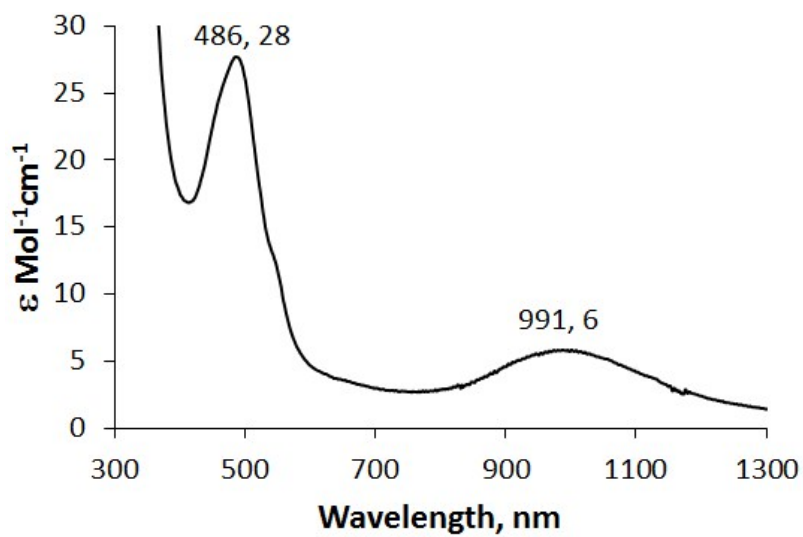


Figure S4. UV-Vis of of Co(II) amine complex **1** in CH_3CN

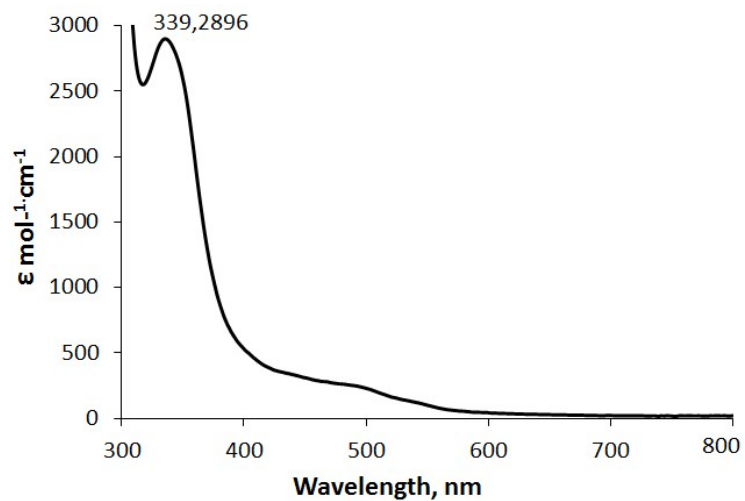


Figure S5. UV-Vis of Co(II) imine complex **2** in CH₃CN

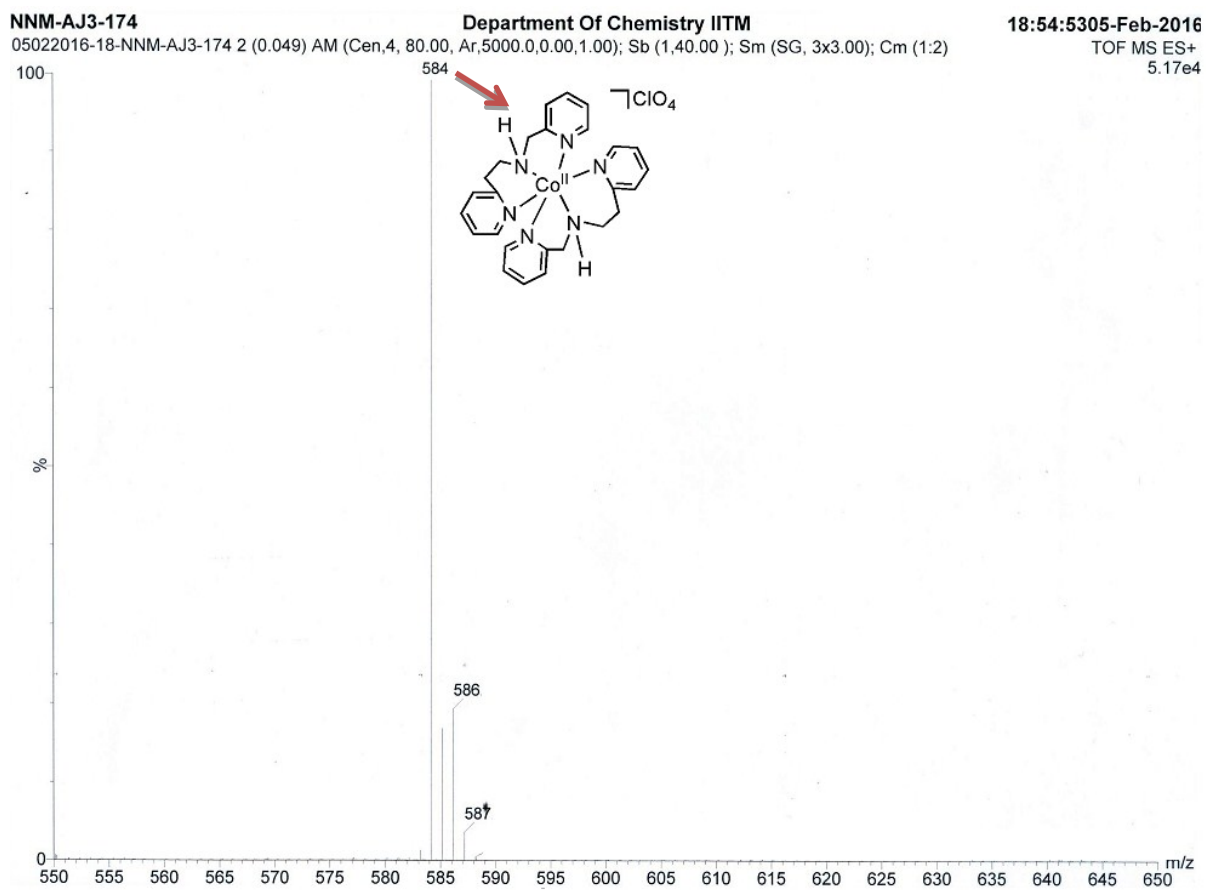


Figure S6. ESI-MS of Co(II) amine complex **1**

NNM-SP4-2B

NNM-SP4-2B 29 (0.286) Sb (1.40.00); Sm (Mn, 2x2.00); Cm (29:38)

Department Of Chemistry IITM

18:22:0111-Mar-2015

TOF MS ES+
1.55e4

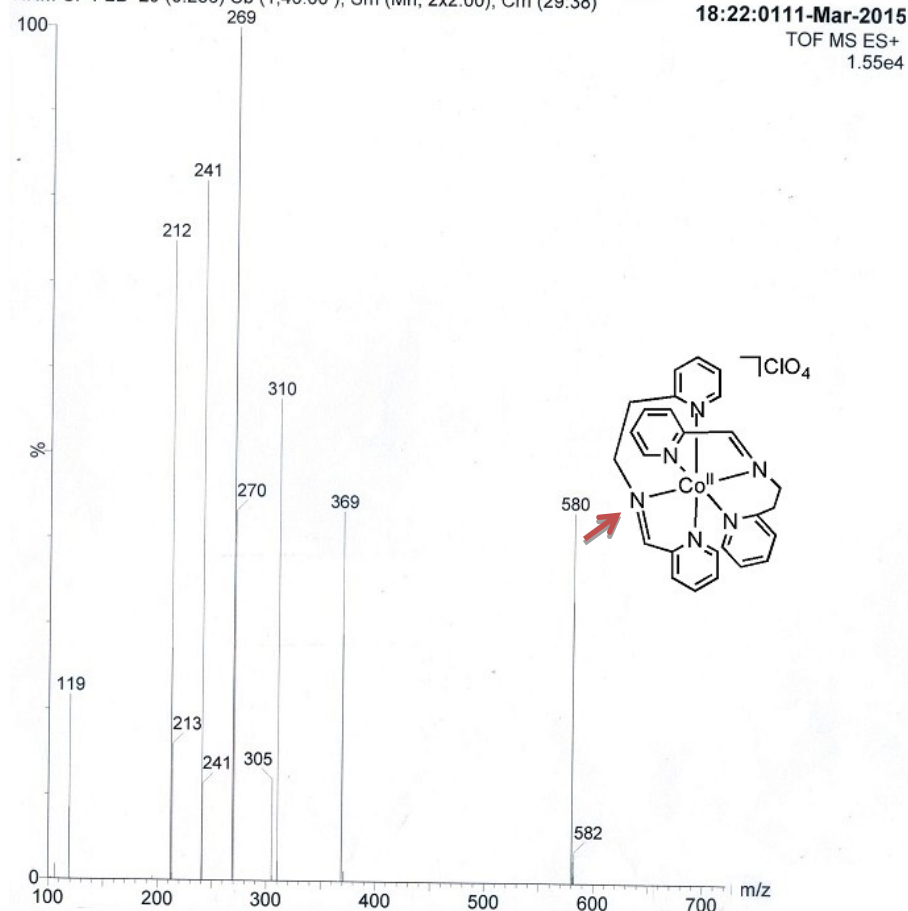
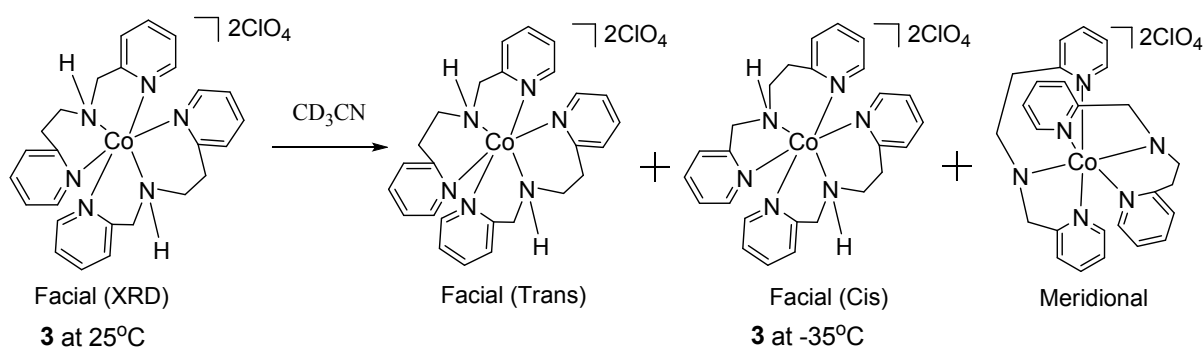


Figure S7. ESI-MS of Co(II) imine complex 2



Scheme S1. Representation of the isomeric forms of 1 expected to exist at 238 K

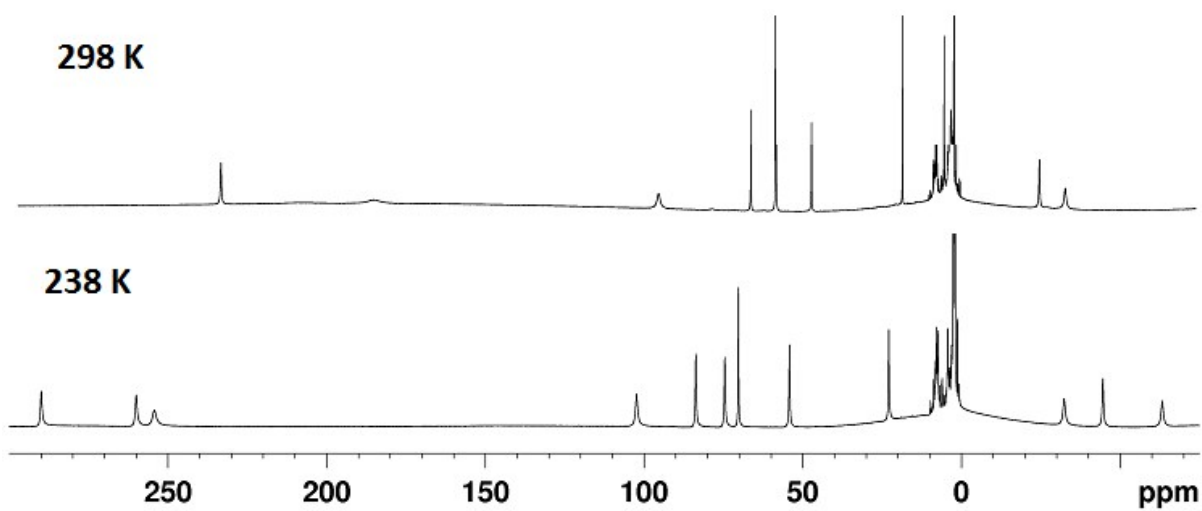


Figure S8. ¹H NMR spectra of Co(II) imine complex **2** in CD₃CN at 298 and 238 K

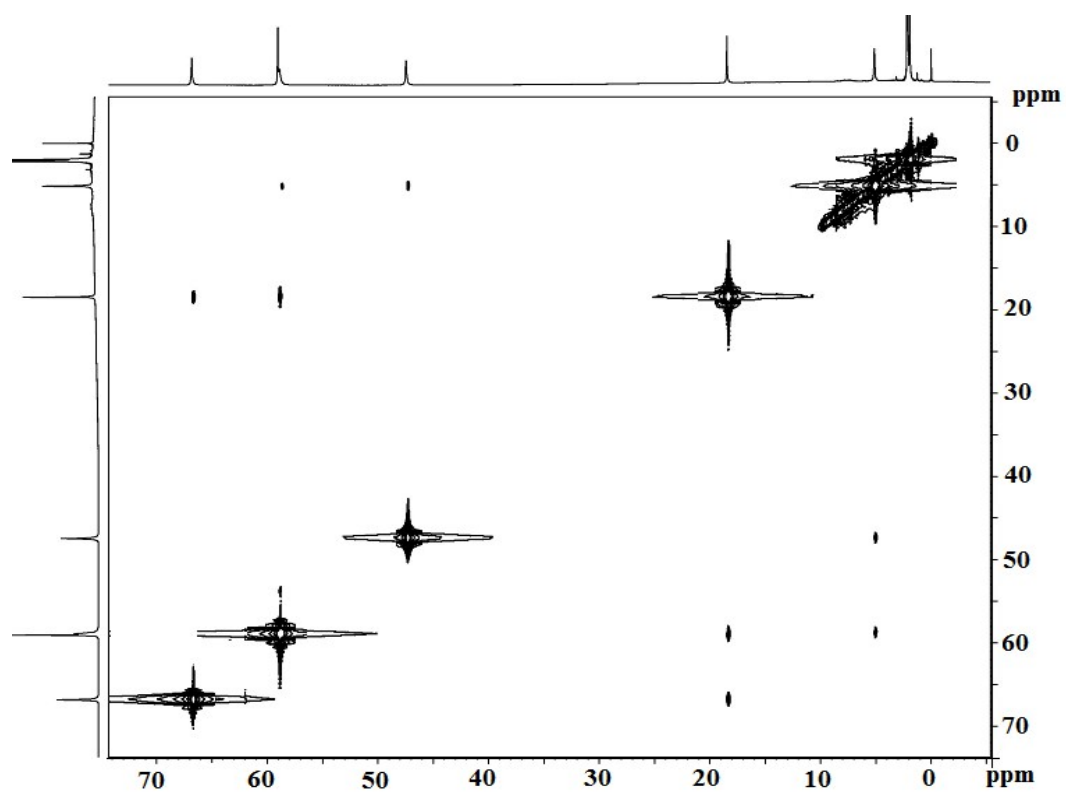


Figure S9. ¹H-¹H COSY of **2** (0 to 80 ppm) in CD₃CN at 298 K

Signal Position, ppm	T1(ms)	Fwh (Hz)	T2(ms)	R _{Co-H} (Å) (X-ray)	R _{Co-H} (Å) (Soln)	Assignment
235.33	6.26	150.55	2.11	3.14 _{av}	3.66	o-Py
96.02	2.94	452.05	0.70	3.69 _{av}	3.23	-CH ₂
66.66	31.81	40.31	7.90	5.17	4.80	m-py
58.86	39.07	25.89	12.30	5.08	4.97	m-py
47.34	46.82	41.05	7.76	5.06	5.12	m-py
18.40	98.28*	23.30	13.66	5.79*	-	p-py
5.16	89.39	30.80	10.33	5.84	5.70	p-py
-25.17	2.89	135.32	2.35	3.75 _{av}	3.22	-CH ₂
-33.37	13.70	272.22	1.16	3.80	4.17	=CH

Table S1. Assignment of resonances in the paramagnetic ¹H NMR spectrum of **2** in CD₃CN at 298 K. $T_2 = 1/\pi(\text{Fwh})$, Fwh is full width at half-height. Calculated $R_{\text{Co-H}} = R_{\text{ref}}(T_1/T_{\text{ref}})^{1/6}$, where R_{ref} and T_{ref} are reference (*) values

Peak Position at -35°C	Assignment
289.87	o-Py
260.06	o-Py
254.36	-CH ₂
102.39	-CH ₂
83.73	m-py
74.59	m-py
70.29	m-py
54.20	m-py
22.90	p-py
4.31	p-py
-32.39	=CH
-44.58	-CH ₂
-63.29	-CH ₂

Table S2. Assignment of resonances in the paramagnetic ¹H NMR spectrum of **2** in CD₃CN at 238 K

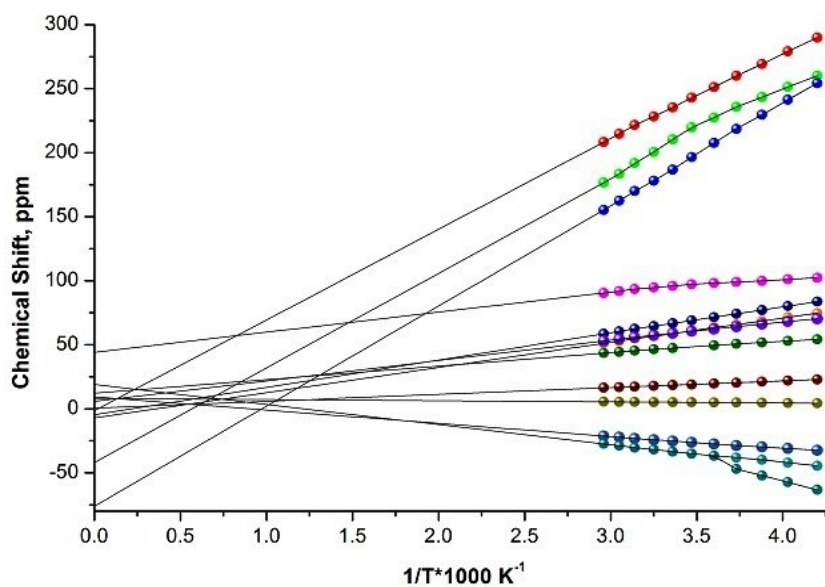


Figure S10. Curie plots showing the temperature dependence of ^1H NMR resonances of **2** in the range 238 -338K

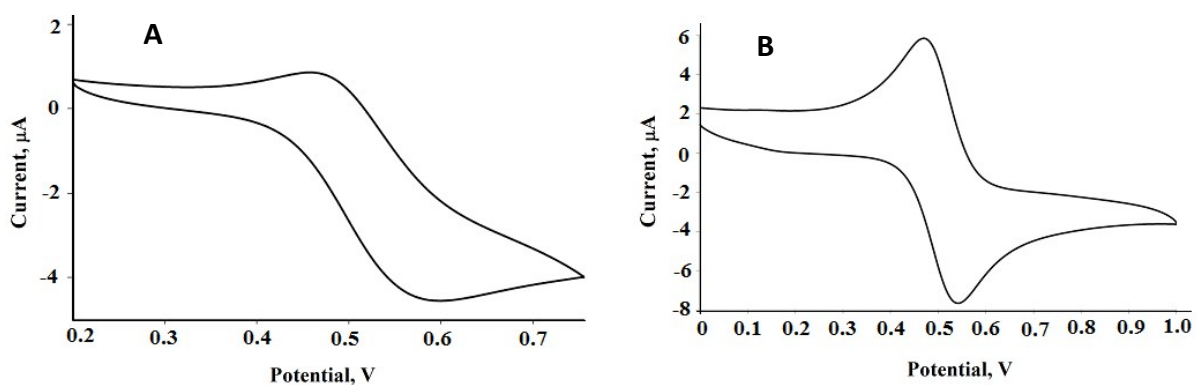


Figure S11. CV of Co(II) amine complex, **1** (A) and imine complex, **2** (B) in CH_3CN

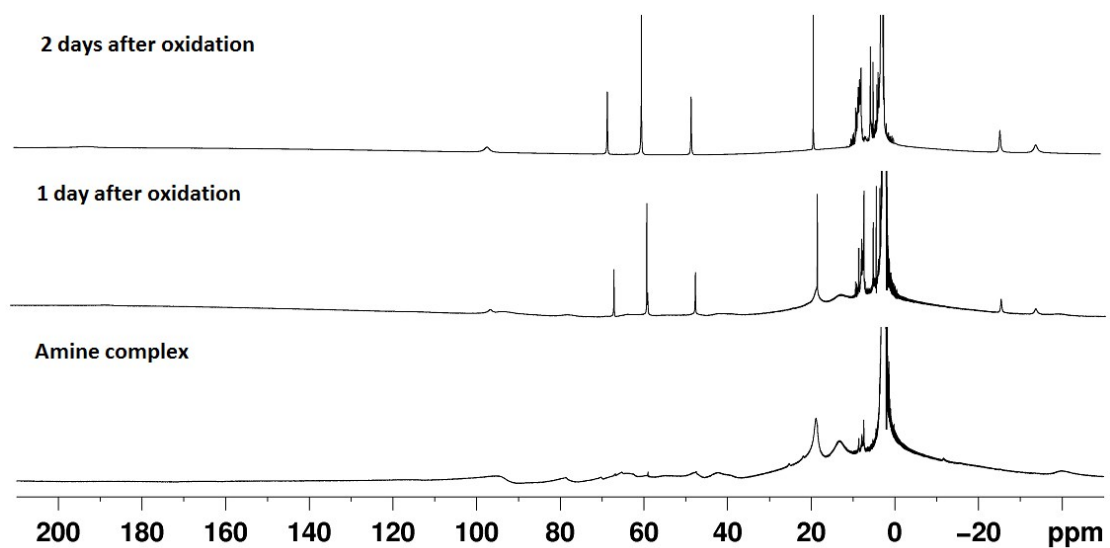


Figure S12. ^1H NMR spectra of Co(II) amine complex **1** in CD_3CN after 24 and 48h of O_2 passage

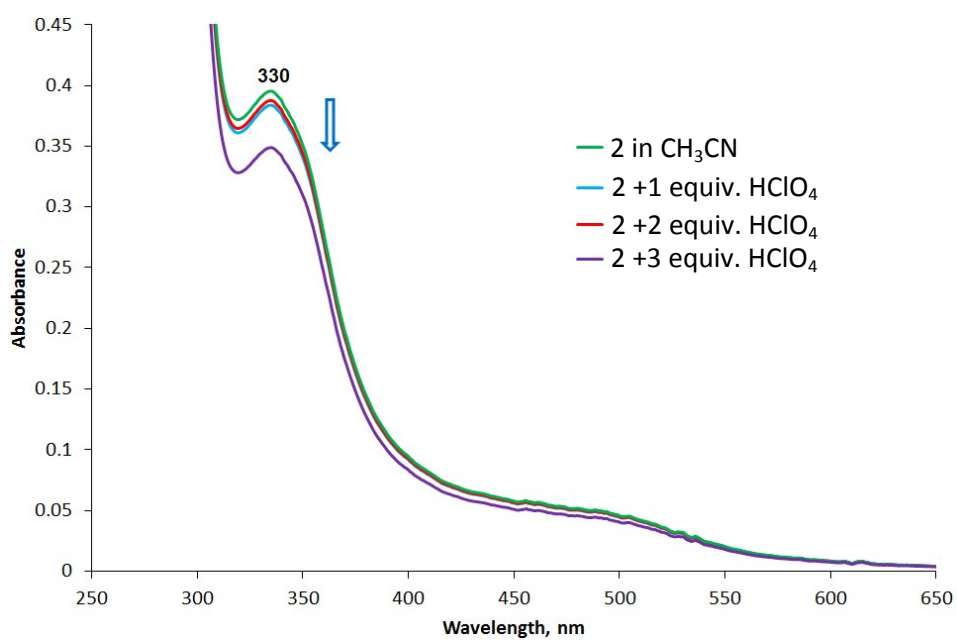


Figure S13. UV-Vis spectra of Co(II) imine complex **2** in CH_3CN in presence of acid, showing its decomposition

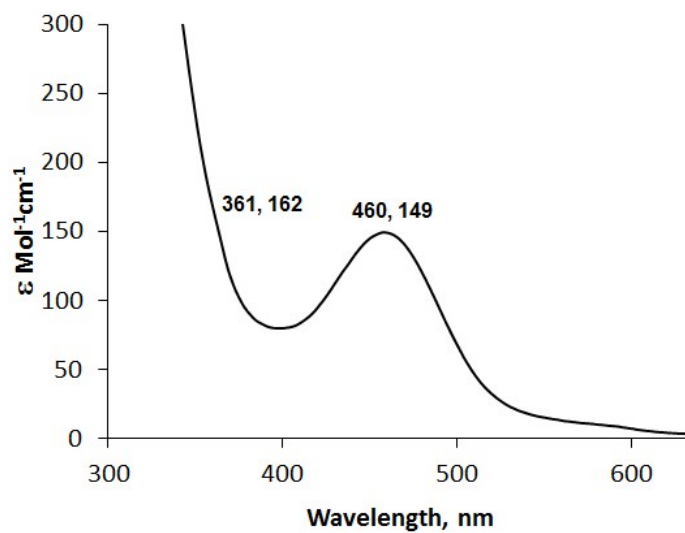


Figure S14. UV-Vis spectra of Co(III) complex 4

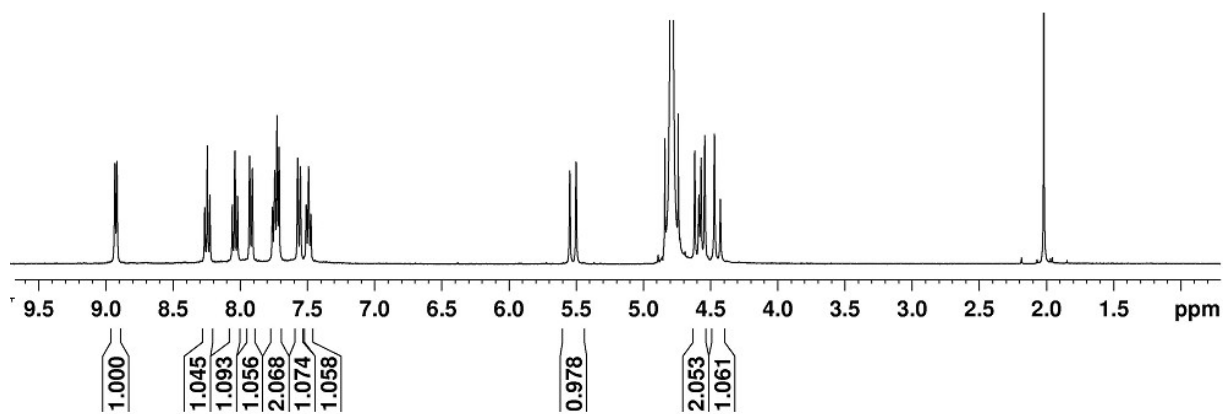


Figure S15. ^1H NMR of Co(III) Complex 4 in D_2O

QTOF MICRO

NNM-AJ2-108 8 (0.149) Sb (3,40.00); Sm (Mn, 2x3.00); Cm (1:53)

09-Oct-2012 16:57:40

TOF MS ES+
7.37e3

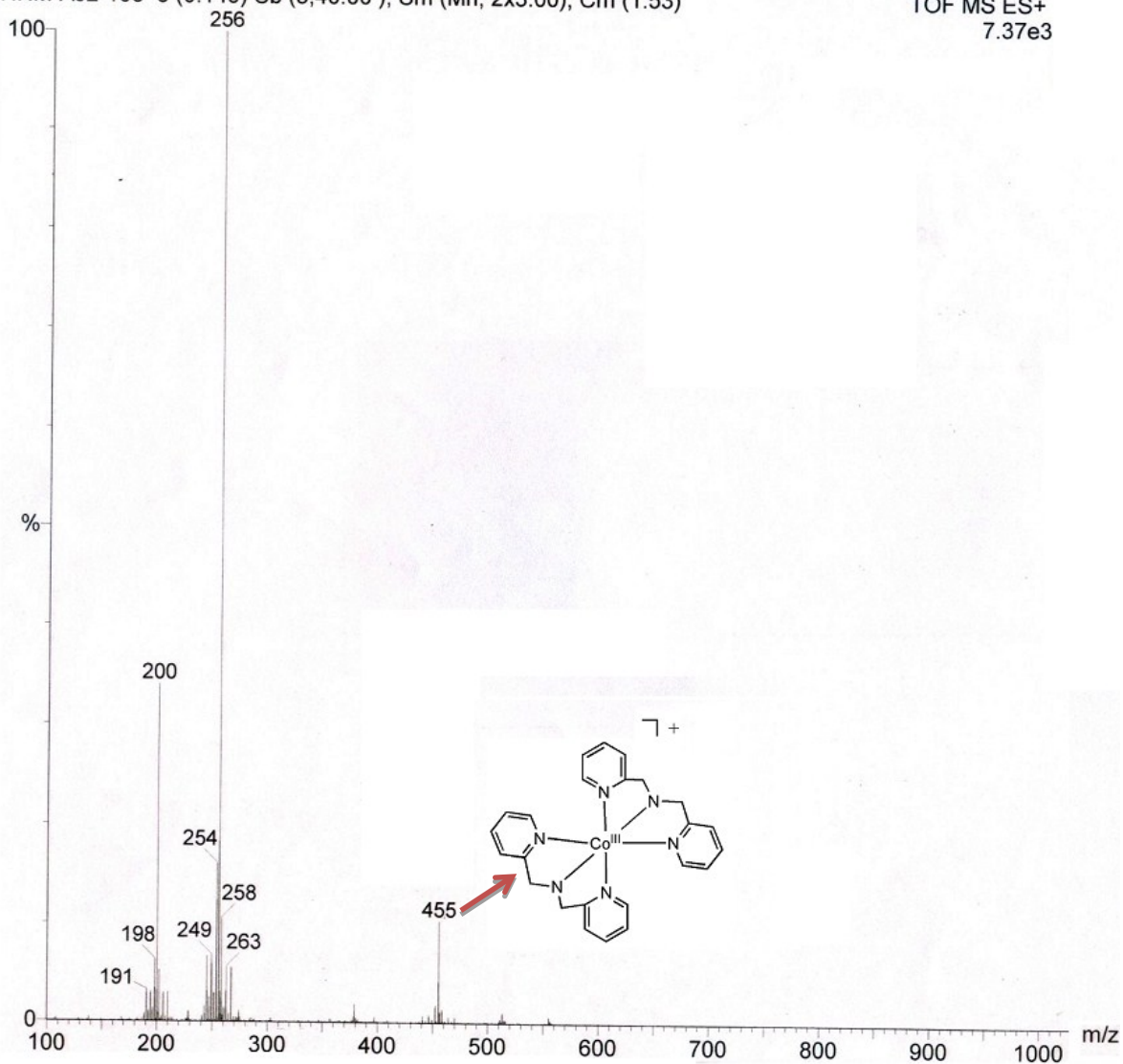


Figure S16. ESI-MS of Co(III) complex 4