Supporting Information

for

Reaction of a Co(III)-peroxo Complex with Nitric Oxide: Putative Formation of a Peroxynitrite Intermediate

Bapan Samanta, Riya Ghosh, Rakesh Mazumdar, Shankhadeep Saha, Sayani Maity, Biplab Mondal*

Department of Chemistry, Indian Institute of Technology Guwahati, Assam 781039, India. Phone: (+)91-361-2582317. Fax: (+)91-361-2582337. Email: biplab@iitg.ac.in.

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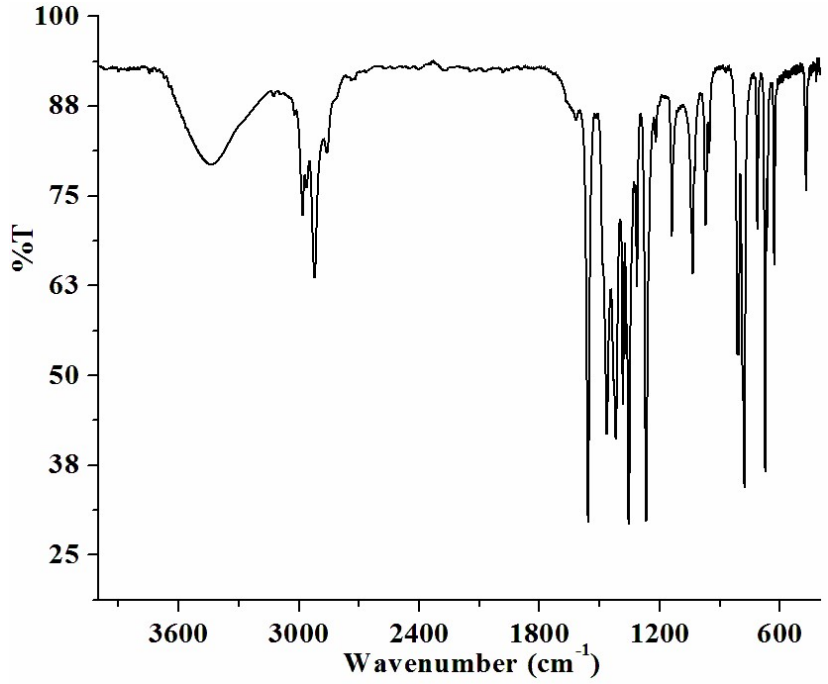

Figure S1. FT-IR spectrum of **L** in KBr.

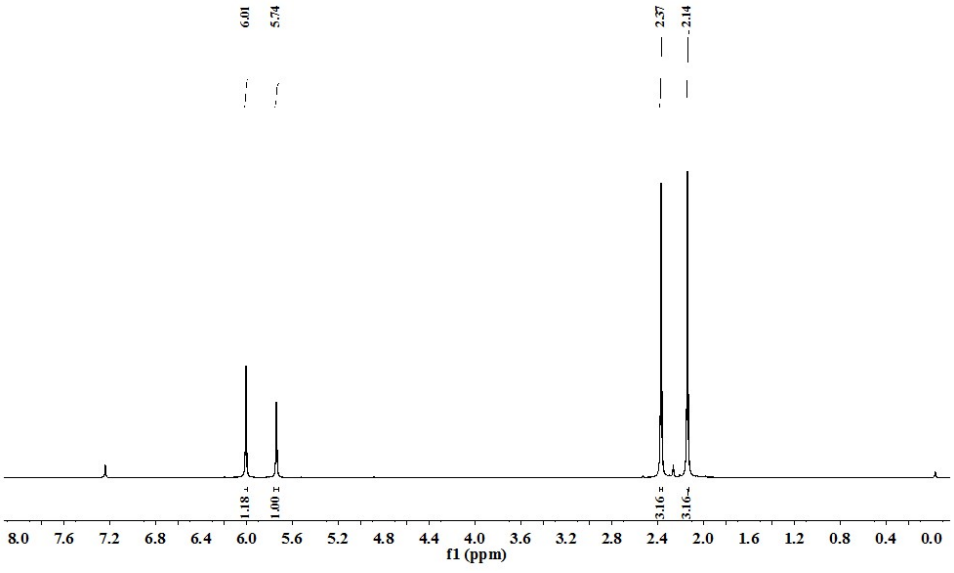

Figure S2. ^{1}H NMR spectrum of **L** in $CDCl_3$.

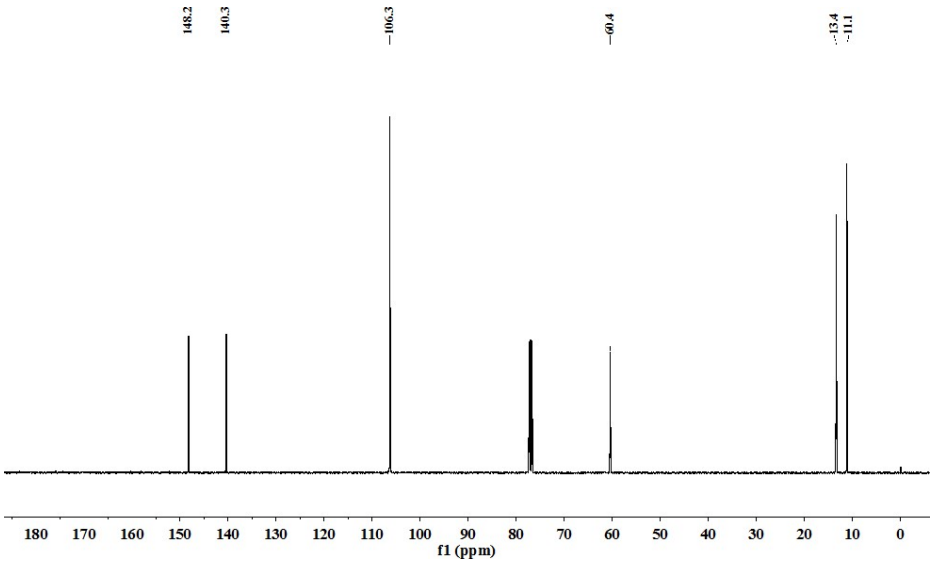

Figure S3. ^{13}C NMR spectrum of **L** in $CDCl_3$.

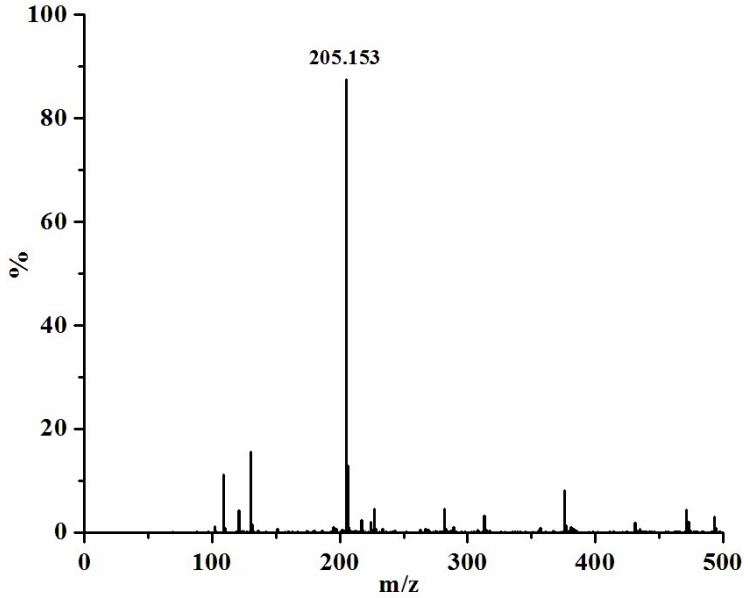

Figure S4. ESI-mass spectrum of **L** in acetonitrile.

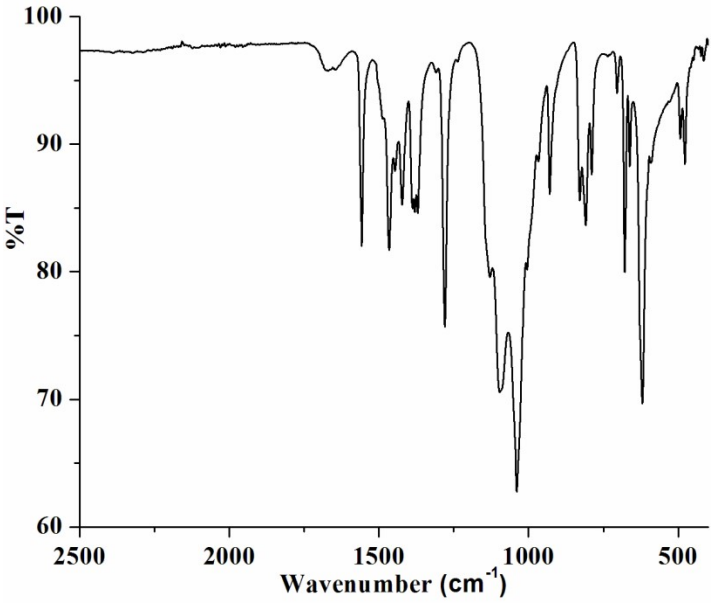

Figure S5. FT-IR spectrum of complex **1** in KBr.

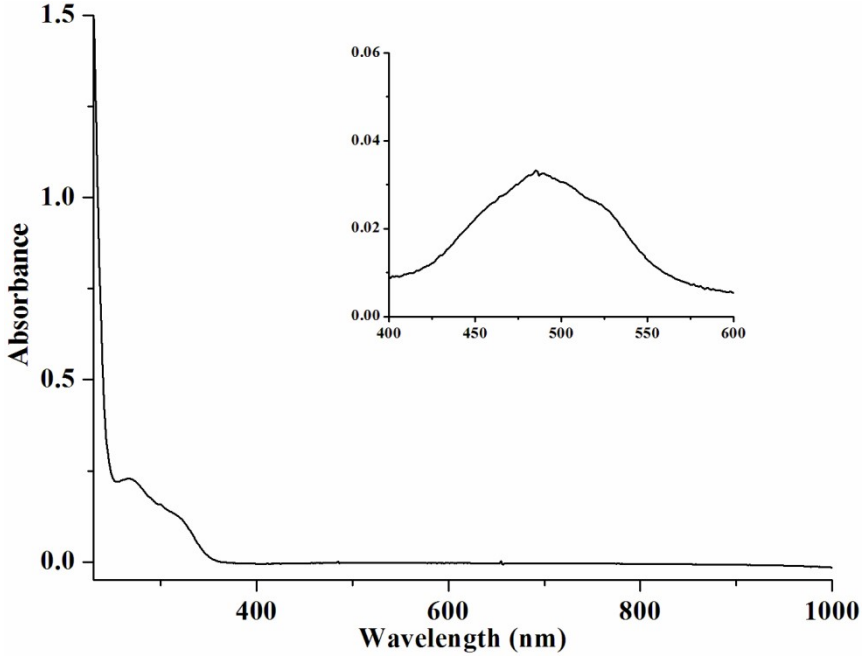

Figure S6. UV-visible spectrum of complex **1** in acetonitrile at room temperature.

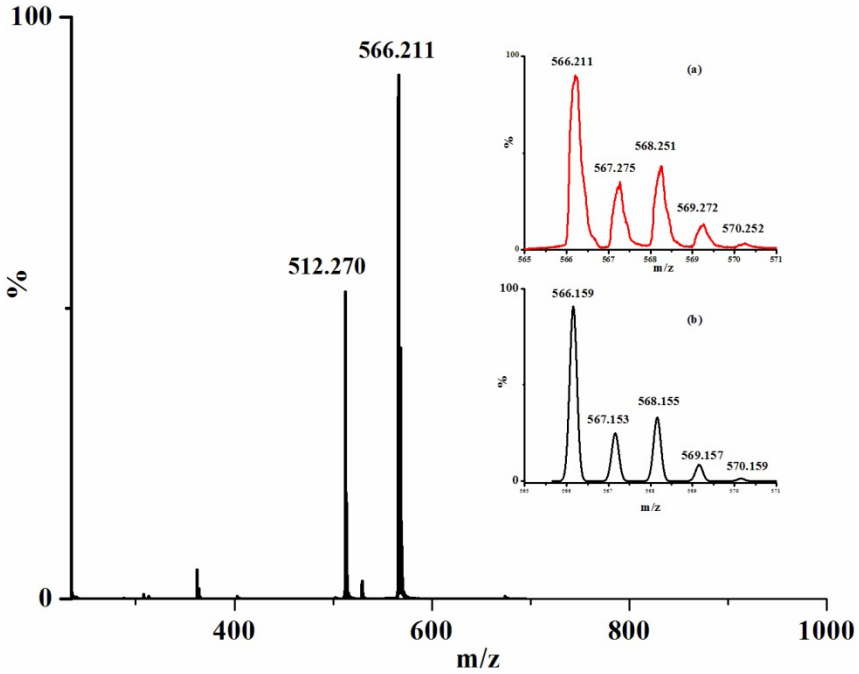

Figure S7. ESI-mass spectrum of complex **1** in acetonitrile. [Inset: (a) experimental and (b) simulated isotopic distribution pattern].

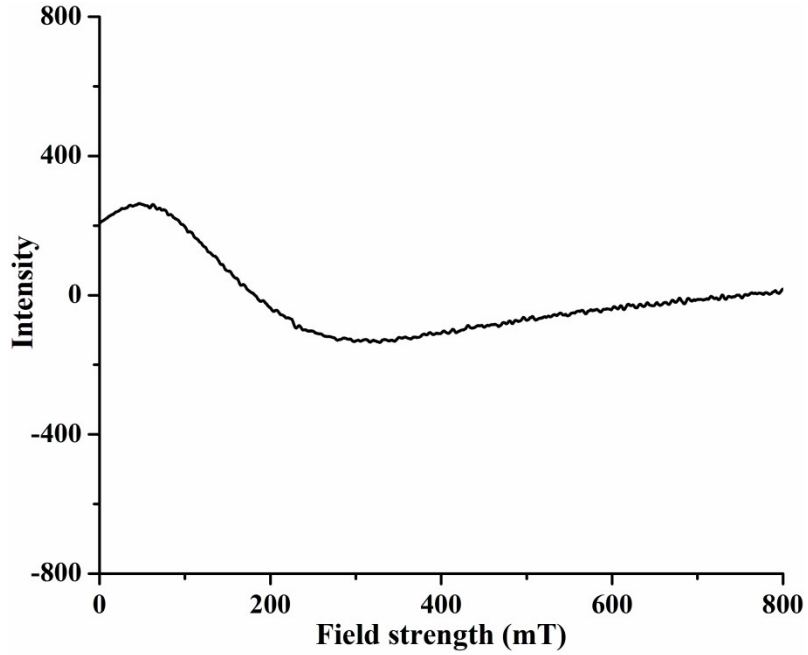

Figure S8. X-band EPR spectrum of complex **1** in acetonitrile at 77K.

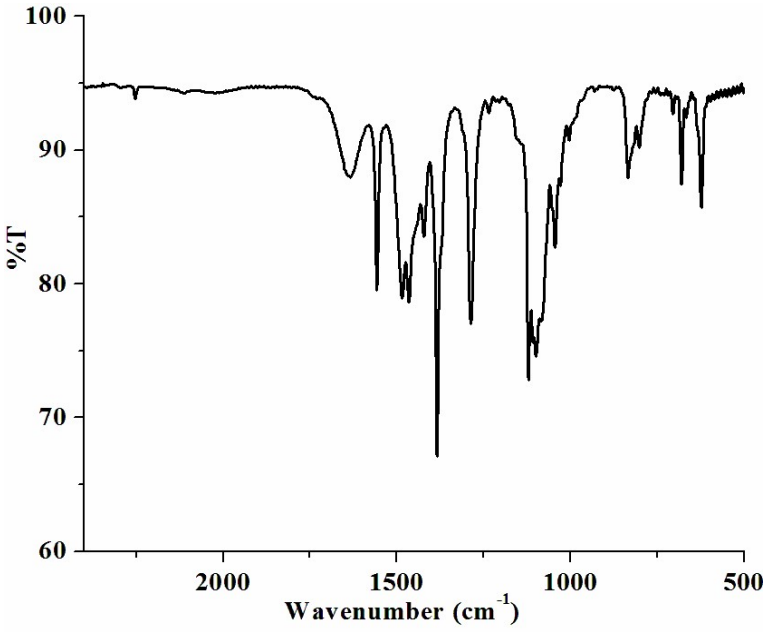

Figure S9. FT-IR spectrum of complex **2** in KBr.

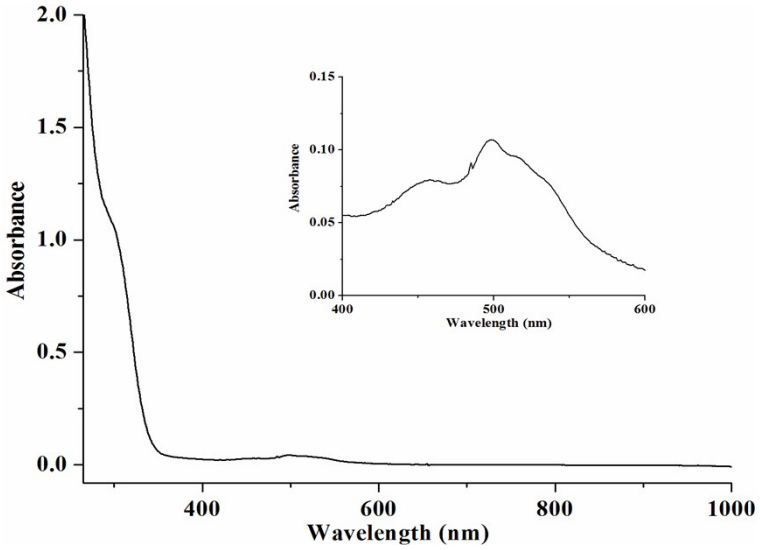

Figure S10. UV-visible spectrum of complex **2** in acetonitrile at room temperature.

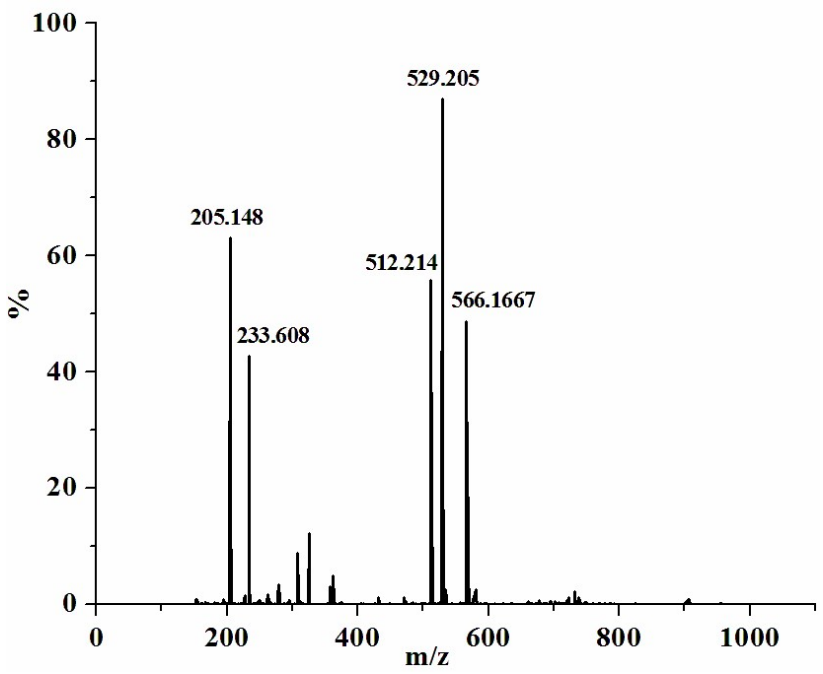

Figure S11. ESI-mass spectrum of complex **2** in acetonitrile.

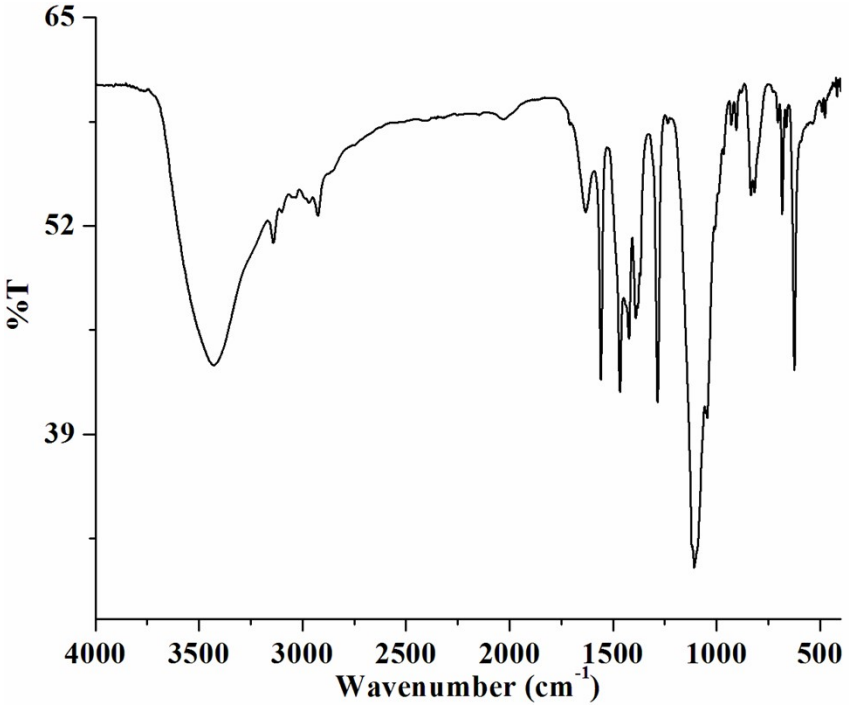

Figure S12. FT-IR spectrum of complex **3** in KBr.

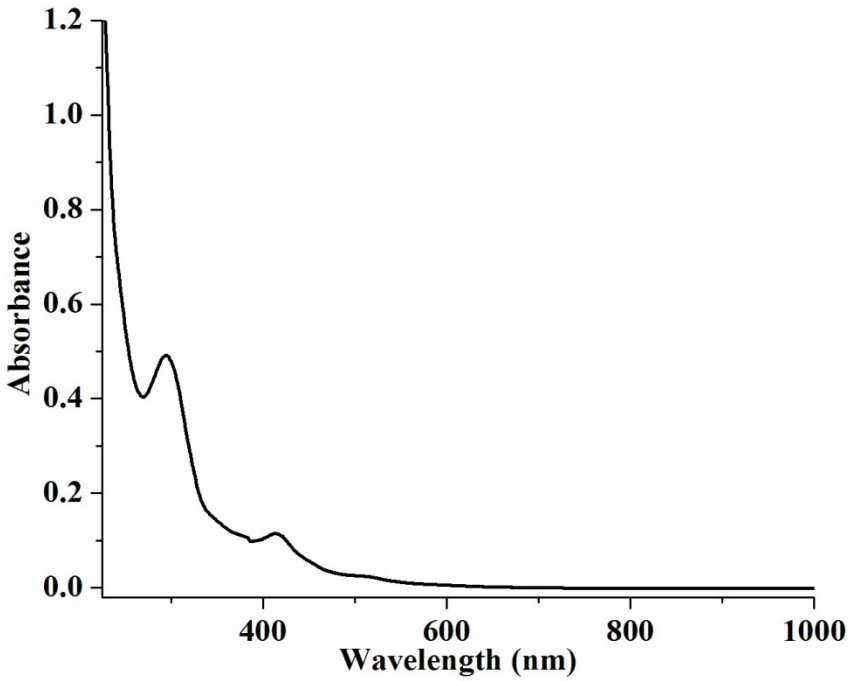

Figure S13. UV-visible spectrum of complex **3** in acetonitrile at room temperature.

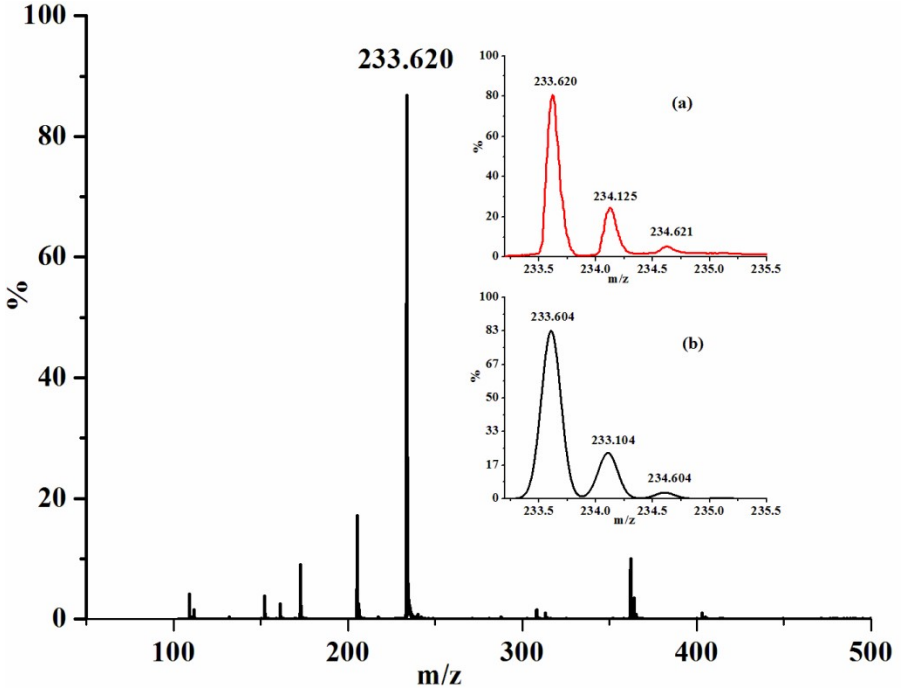

Figure S14. ESI-mass spectrum of complex **3** in acetonitrile. [Inset: (a) experimental and (b) simulated isotopic distribution pattern].

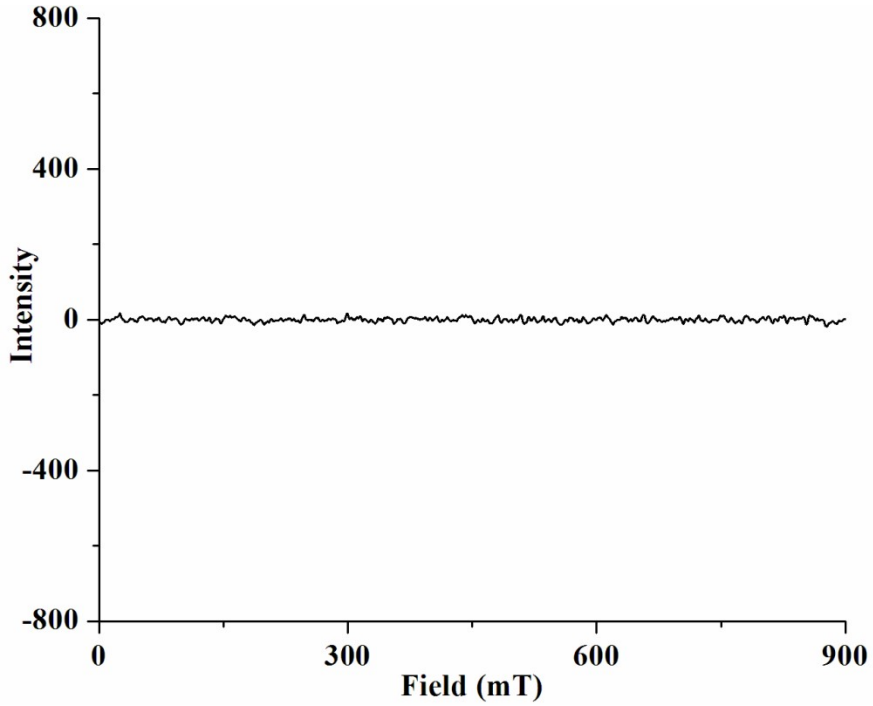

Figure S15. X-band EPR spectrum of complex **3** in acetonitrile at 77K.

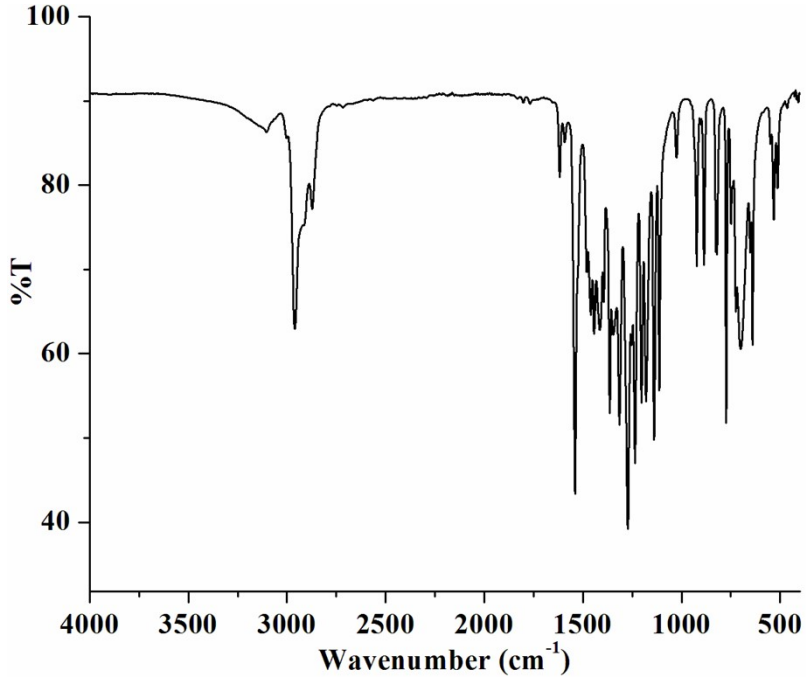

Figure S16. FT-IR spectrum of complex **2,4-di-*tert*-butyl-6-nitrophenol**.

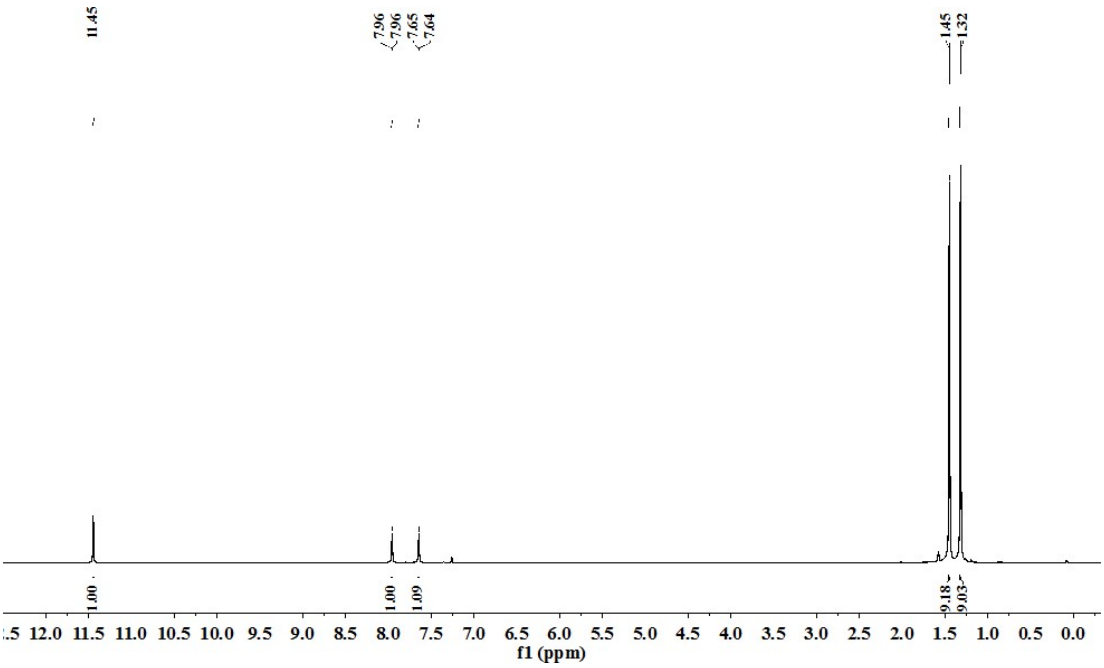

Figure S17. ^{1}H NMR spectrum of **2,4-di-*tert*-butyl-6-nitrophenol** in $CDCl_3$.

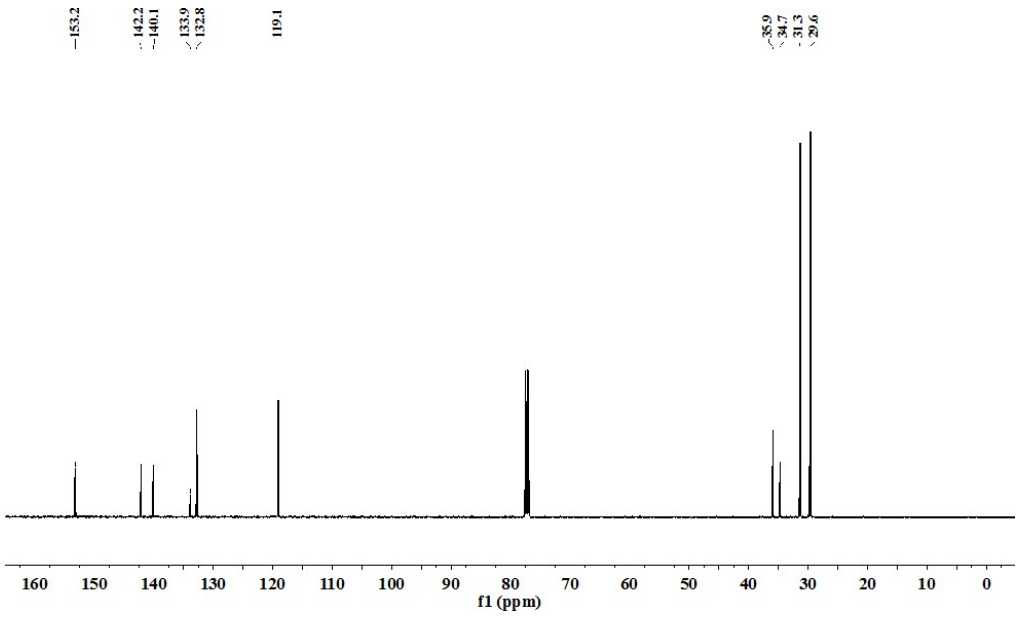

Figure S18. ^{13}C NMR spectrum of **2,4-di-*tert*-butyl-6-nitrophenol** in $CDCl_3$.

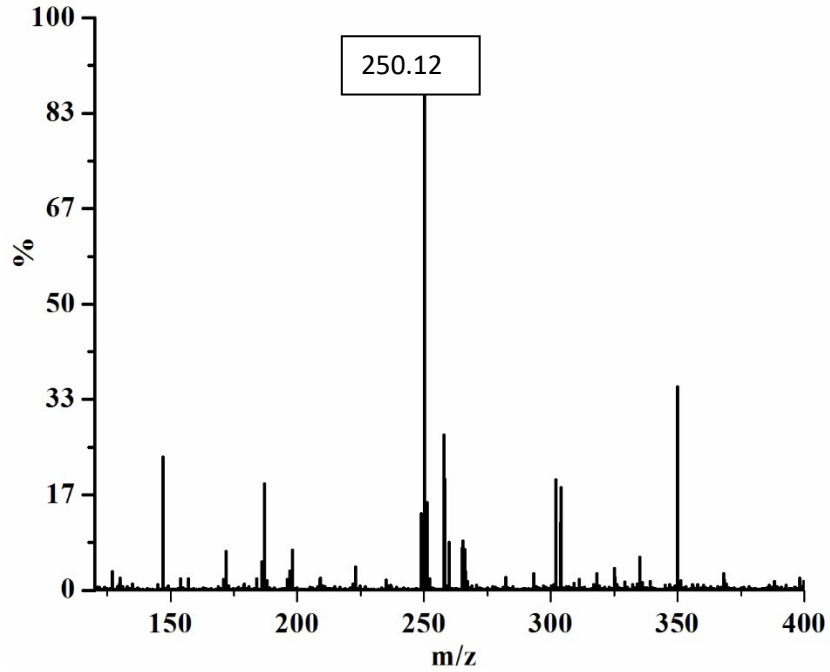

Figure S19. ESI-mass spectrum of **2,4-di-*tert*-butyl-6-nitrophenol** in acetonitrile.

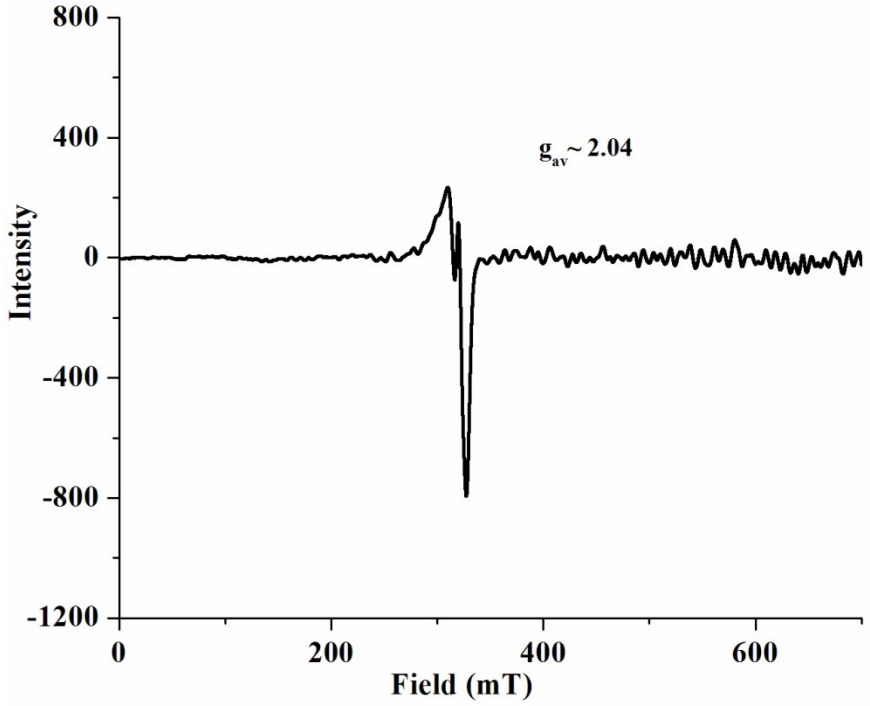

Figure S20. X-band EPR spectrum of Cobalt(II)-hydroxide complex in acetonitrile at 77K.

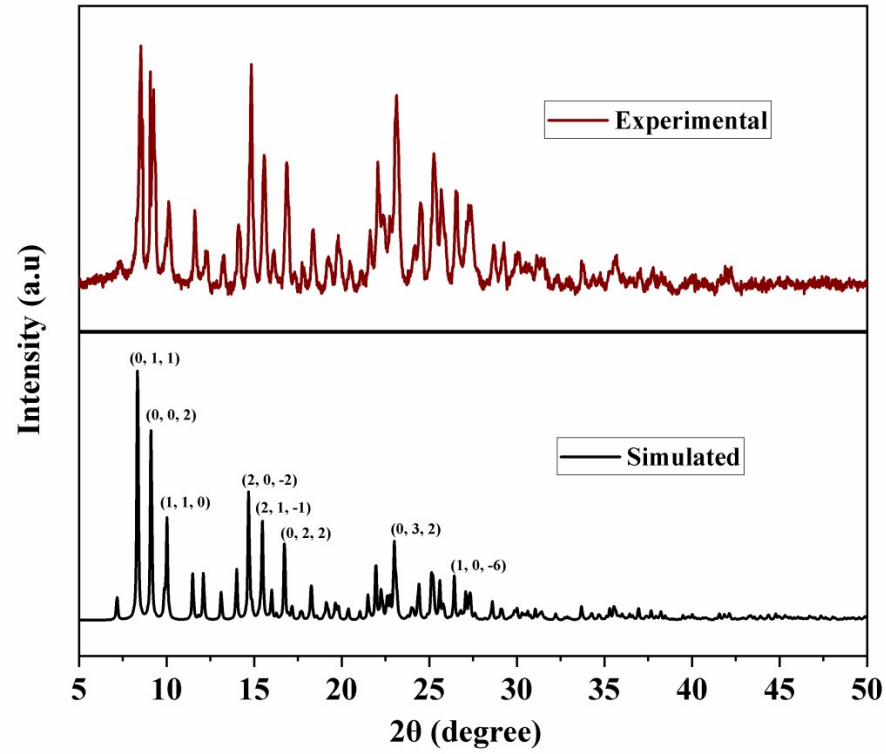

Figure 21. Experimental (red) and Simulated (black) PXRD patterns of complex **1**.

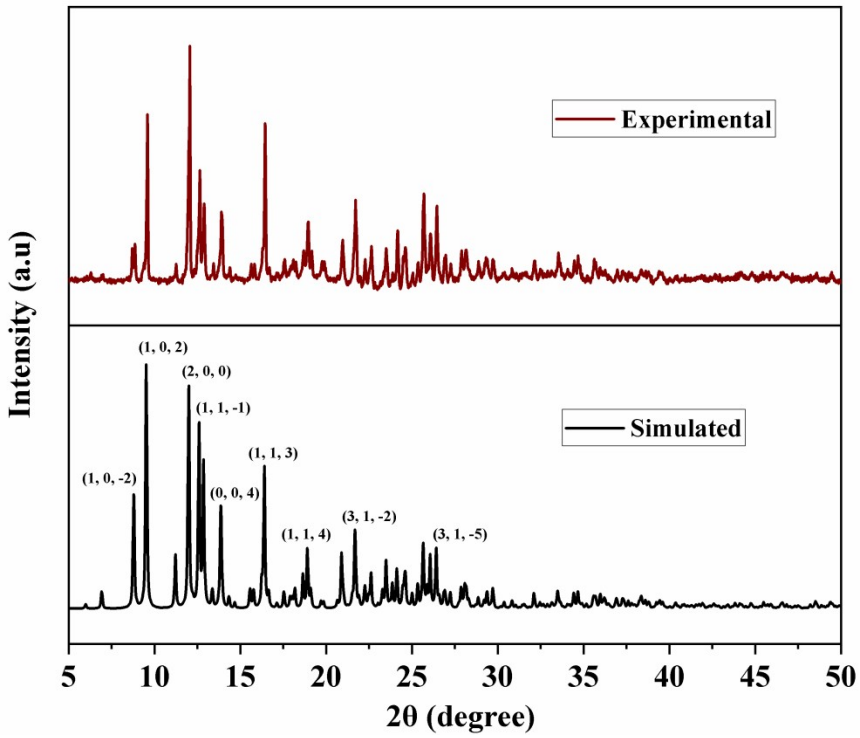

Figure 22. Experimental (red) and Simulated (black) PXRD patterns of complex **2**.

Table A1: Crystallographic data for complexes **1** and **2**.

	Complex 1	**Complex 2**
Formulae	$C_{22}H_{36}CoN_8O_{10}Cl_2$	$C_{24}H_{35}CoN_{10}O_7Cl$
Mol. Wt	702.42	670
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
Temperature/K	296	296
Wavelength/Å	0.71073	0.71073
a/ Å	12.8427(6)	14.7963(8)
b/ Å	12.6406(6)	8.2883(4)
c/ Å	20.2239(9)	25.5819(13)
α/	90	90.00
β/	106.4850(10)	94.607(2)
γ/	90	90.00
V/ Å^3	3148.2(3)	3127.1(3)
Z	4	4
Density/Mgm^{-3}	1.482	1.423
Abs. Coeff. /mm^{-1}	0.778	0.692
Abs. Correction	Multi-scan	Multi-scan
F(000)	1460.0	1396.0
Total no. of reflections	5534	5508
Reflections. $I > 2\sigma(I)$	4352	4464
Max. 2θ/	24.999	24.999
Ranges (h, k, l)	$-15 \le h \le 15$ $-15 \le k \le 15$ $-24 \le l \le 24$	$-17 \le h \le 17$ $-9 \le k \le 9$ $-30 \le l \le 30$
Complete to 2θ (%)	99	100
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goof(F^2)	1.013	1.102
R indices [$I > 2\sigma(I)$]	0.0560	0.0532
R indices (all data)	0.0736	0.0703
Residual electron density	0.73	0.54

Table A2: Selected bond lengths (Å) of complexes **1** and **2.**

Atoms	Complex 1	Complex 2
Co1-N1	2.136(3)	2.106(3)
Co1-N4	2.130(3)	2.116(3)
Co1-N5	2.118(3)	2.100(3)
Co1-N8	2.126(3)	2.110(3)
Co1-O1	2.206(3)	2.217(2)
Co1-O2	2.180(3)	2.192(2)
N1-N2	1.362(4)	1.368(4)
N3-N4	1.370(4)	1.364(4)
N2-C6	1.441(5)	1.446(4)
N3-C6	1.447(5)	1.447(4)
N9-O1	-	1.260(4)
N9-O2	-	1.263(3)
N9-O3	-	1.228(4)

Table A3: Selected bond angles (°) of complexes **1** and **2**.

Atoms	Complex 1	Complex 2
N1-Co1-O1	88.36(12)	160.14(10)
N1-Co1-O2	88.84(13)	101.85(10)
N1-Co1-N4	88.70(12)	88.66(10)
N1-Co1-N8	175.87(13)	97.09(11)
N1-Co1-N5	93.33(12)	96.66(11)
N4-Co1-N5	91.48(13)	95.73(11)
N4-Co1-N8	95.23(12)	172.38(11)
N4-Co1-O1	172.64(12)	87.90(10)
N4-Co1-O2	93.62(14)	86.22(10)
N1-C2-C1	122.5(4)	122.6(3)
N1-C2-C3	109.6(4)	109.2(3)
N1-N2-C4	111.6(3)	
N2-C4-C3	105.7(4)	106.5(3)
N2-C4-C5	123.0(4)	123.2(4)
N1-N2-C6	119.5(3)	118.6(3)
N2-C6-N3	111.2(3)	110.7(3)
N4-N3-C6	119.1(3)	118.2(3)

N2-N1-Co1	118.7(2)	120.0(2)
N3-N4-Co1	119.7(2)	
C2-C3-C4	107.5(4)	
C1-C2-C3	127.9(4)	
N5-Co1-N8		88.59(11)
N5-Co1-O2		161.44(10)
N1-Co1-O2		101.85(10)
N8-Co1-O2		87.70(10)
N4-Co1-O2		87.90(10)
N8-Co1-O1		85.00(10)
O2-Co1-O1		58.41(9)
O1-N9-O3		121.8(3)
O2-N9-O3		121.2(3)
O1-N9-O2		117.0(3)