

Supporting Information

Inter-Ligand Azo (N=N) Unit Formation and Thereafter Stabilization of A Co(II)–Diradical Complex *via* Metal-to-Ligand $d\pi-p\pi$ back donation: Synthesis, Characterization, and Theoretical Study**

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Materials:

All the chemicals and solvents were obtained from commercial sources and were used as supplied, unless noted otherwise. 3,5-di-*tert*-butylcatechol, was purchased from Sigma–Aldrich. Solvents were obtained from Merck (India). phthalic anhydride was purchased from Merck (India).

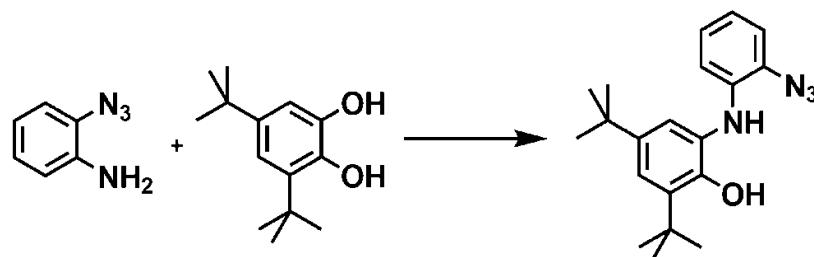
Physical Methods:

X–ray crystallographic data were collected using Super Nova, Single source at offset, Eos diffractometer. Structures were solved by direct methods using SHELXS–97 and refined with full-matrix least squares on F^2 using SHELXL–97. All the non–hydrogen atoms were refined anisotropically.

IR spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). UV–vis/NIR spectra were recorded on Perkin Elmer, Lamda 750, UV/VIS/NIR spectrometer preparing a known concentration of the samples in HPLC Grade CH_2Cl_2 at room temperature using cuvette of 1 cm width. EPR spectra were measured on X–Band Microwave Unit, JES–FA200 ESR spectrometer at 77 K. Mass spectral data were obtained from either HRMS or QTOF MS Spectrometer. Variable-temperature magnetic susceptibility measurements were performed using SQUID magnetometer at 0.1T.

Experimental Section:

Synthesis of 2-azidoaniline has already been reported.¹



Synthesis of [C₂₀H₂₆N₄O], H₂Rich(AP)^{N₃}: To a solution of 3,5-di-*tert*-butylcatechol (2.58 g, 11.64 mmol) and 2-azidoaniline (1.56g, 11.64 mmol) in hexane (25 mL), Et₃N (0.05 mL) was added and the resulting solution was stirred for 48 h at room temperature (30 °C). During this period a brown precipitate appeared which was recrystallized from methanol giving colourless crystalline solid. This solid was washed twice with methanol (5 mL) and then, dried under high vacuum. Yield: 2.37 g, 60%. FTIR (KBr pellet cm⁻¹): 3424, 3348, 2955, 2901, 2867, 2131, 2093, 1592, 1501, 1480, 1419, 1359, 1293, 1218, 1197, 1146, 1117, 1090, 1042, 969, 882, 825, 806, 764, 744, 610. ¹H NMR (CDCl₃, 399.85 MHz): δ 7.23 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.98–6.94 (m, 2H), 6.87 (td, *J* = 7.6, 1.6 Hz, 1H), 6.42 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.28 (s, 1H), 5.38 (s, 1H), 1.44 (s, 9H), 1.26 (s, 9H) ppm. ¹³C NMR (CDCl₃, 100.55 MHz): δ 149.8, 142.5, 138.6, 135.6, 127.1, 126.2, 125.9, 122.5, 121.8, 120.0, 118.2, 114.7, 35.2, 34.6, 31.8, 29.7 ppm. Anal. Calcd for C₂₀H₂₆N₄O: C, 70.96; H, 7.75; N, 16.56. Found: C, 71.49; H, 7.86; N, 16.55. ESI-MS (+) *m/z* for [C₂₀H₂₆N₄O+H]⁺: calcd, 339.2179; found, 339.2175.

Synthesis of [C₄₀H₄₉ClCoN₄O₂], 1: To a solution of H₂Rich(AP)^{N₃} (0.338 g, 1 mmol) in acetonitrile (10 mL), CoCl₂•6H₂O (0.238 g, 1 mmol) was added followed by addition of Et₃N (0.2 mL). The resulted solution was stirred for 2 h at room temperature under air. A brown-black precipitate appeared which was washed with acetonitrile (5 mL) and then with diethylether (5 mL). Recrystallization of the solid from a dichloromethane/acetonitrile (5:1) solvent mixture afforded a crystalline compound that was suitable for single crystal X-ray diffraction measurement. Yield: 75 mg, 21%. FTIR (KBr pellet cm⁻¹): 3243, 2955, 2905, 2867, 1583, 1522, 1479, 1385, 1359, 1310, 1248, 1201, 1099, 1028, 996, 912, 755. Anal. Calcd for C₄₀H₄₉ClCoN₄O₂•1.5H₂O: C, 65.01; H, 7.10; N, 7.58. Found: C, 64.70; H, 6.71; N, 7.60. ESI-MS (+) *m/z* for [C₄₀H₄₉CoN₄O₂]⁺: calcd, 676.3187; found, 676.3159.

Table 1. Selected bond distances (Å) and bond angles (°) for **1**, [C₄₀H₄₉ClCoN₄O₂].

Co1–N1	1.861(2)	N1–Co1–N4	161.09(11)
Co1–N2	1.849(2)	N1–Co1–O1	83.06(10)
Co1–N4	1.862(2)	N1–Co1–Cl1	101.55(8)
Co1–O1	1.890(2)	N1–C1–C2	110.1(2)
Co1–Cl1	2.3217(10)	N2–Co1–N1	84.88(10)
N1–C1	1.355(4)	N2–Co1–N4	93.00(11)
N1–C7	1.401(4)	N2–Co1–O1	163.62(10)
N2–C12	1.434(4)	N2–Co1–Cl1	94.09(8)
N2–N3	1.282(3)	N2–N3–C13	119.0(3)
N3–C13	1.365(4)	N3–N2–Co1	132.5(2)
N4–C18	1.361(4)	N3–C13–C18	127.0(3)
N4–C19	1.449(4)	N4–Co1–O1	94.82(10)
O1–C2	1.302(3)	N4–Co1–Cl1	97.34(8)
O2–C24	1.364(4)	N4–C18–C13	121.9(3)
C1–C6	1.411(4)	O1–Co1–Cl1	99.15(7)
C2–C1	1.434(4)	O1–C2–C1	116.6(3)
C2–C3	1.423(4)	C2–O1–Co1	113.77(18)
C3–C4	1.378(4)	C1–N1–Co1	116.31(19)
C5–C4	1.421(4)	C7–N1–Co1	114.22(19)
C5–C6	1.357(4)	C7–C12–N2	113.5(3)
C7–C8	1.391(4)	C12–C7–N1	112.2(2)
C8–C9	1.374(4)	C12–N2–Co1	112.89(18)
C9–C10	1.383(5)	C18–N4–Co1	124.0(2)
C11–C10	1.379(4)	N1–Co1–N4	161.09(11)
C12–C7	1.401(4)	N1–Co1–O1	83.06(10)
C12–C11	1.372(4)	N1–Co1–Cl1	101.55(8)
C13–C14	1.410(4)	N1–C1–C2	110.1(2)
C13–C18	1.426(4)	N2–Co1–N1	84.88(10)
C14–C15	1.353(4)	N2–Co1–N4	93.00(11)
C15–C16	1.390(5)	N2–Co1–O1	163.62(10)
C17–C16	1.361(5)	N2–Co1–Cl1	94.09(8)
C18–C17	1.429(4)	N2–N3–C13	119.0(3)
C19–C20	1.379(4)	N3–N2–Co1	132.5(2)
C19–C24	1.392(4)	N3–C13–C18	127.0(3)
C20–C21	1.378(4)	N4–Co1–O1	94.82(10)
C21–C22	1.391(5)	N4–Co1–Cl1	97.34(8)
C22–C23	1.388(5)	N4–C18–C13	121.9(3)
C24–C23	1.401(4)	O1–Co1–Cl1	99.15(7)
C7–C12–N2	113.5(3)	O1–C2–C1	116.6(3)
C12–C7–N1	112.2(2)	C2–O1–Co1	113.77(18)
C12–N2–Co1	112.89(18)	C1–N1–Co1	116.31(19)
C18–N4–Co1	124.0(2)	C7–N1–Co1	114.22(19)

Table 2. Crystallographic data and structure refinement parameters for **1**, [C₄₀H₄₉ClCoN₄O₂].

Empirical formula	C ₄₀ H ₄₉ ClCoN ₄ O ₂
Formula weight	712.21
CCDC Number	CCDC 990520
Crystal habit, colour	block/ brown
Crystal size, mm ³	0.34 X 0.28 X 0.22
Temperature, <i>T</i>	293(2) K
Wavelength, λ (Å)	0.71073
Crystal system	triclinic
Space group	' <i>P</i> -1'
Unit cell dimensions	$a = 9.3974(4)$ Å $b = 11.8652(4)$ Å $c = 17.5161(10)$ Å $\alpha = 101.422(4)^\circ$, $\gamma = 89.970(3)^\circ$, $\beta = 92.112(4)^\circ$
Volume, V (Å ³)	1913.06(15)
<i>Z</i>	2
Calculated density, Mg·m ⁻³	1.236
Absorption coefficient, μ (mm ⁻¹)	0.556
<i>F</i> (000)	754
θ range for data collection	2.92° to 25.00°
Limiting indices	-11 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 14, -20 ≤ <i>l</i> ≤ 11
Reflection collected / unique	12293/ 6716 [<i>R</i> (int) = 0.0306]
Completeness to θ	99.8% ($\theta = 25.00^\circ$)
Max. and min. transmission	0.885/ 0.830
Refinement method	'SHELXL-97 (Sheldrick, 1997)'
Data / restraints / parameters	6716 / 0 / 446
Goodness-of-fit on F^2	1.023
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0499, <i>wR</i> 2 = 0.1054
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0753, <i>wR</i> 2 = 0.1198
Largest diff. peak and hole	0.462 and -0.268 e·Å ⁻³

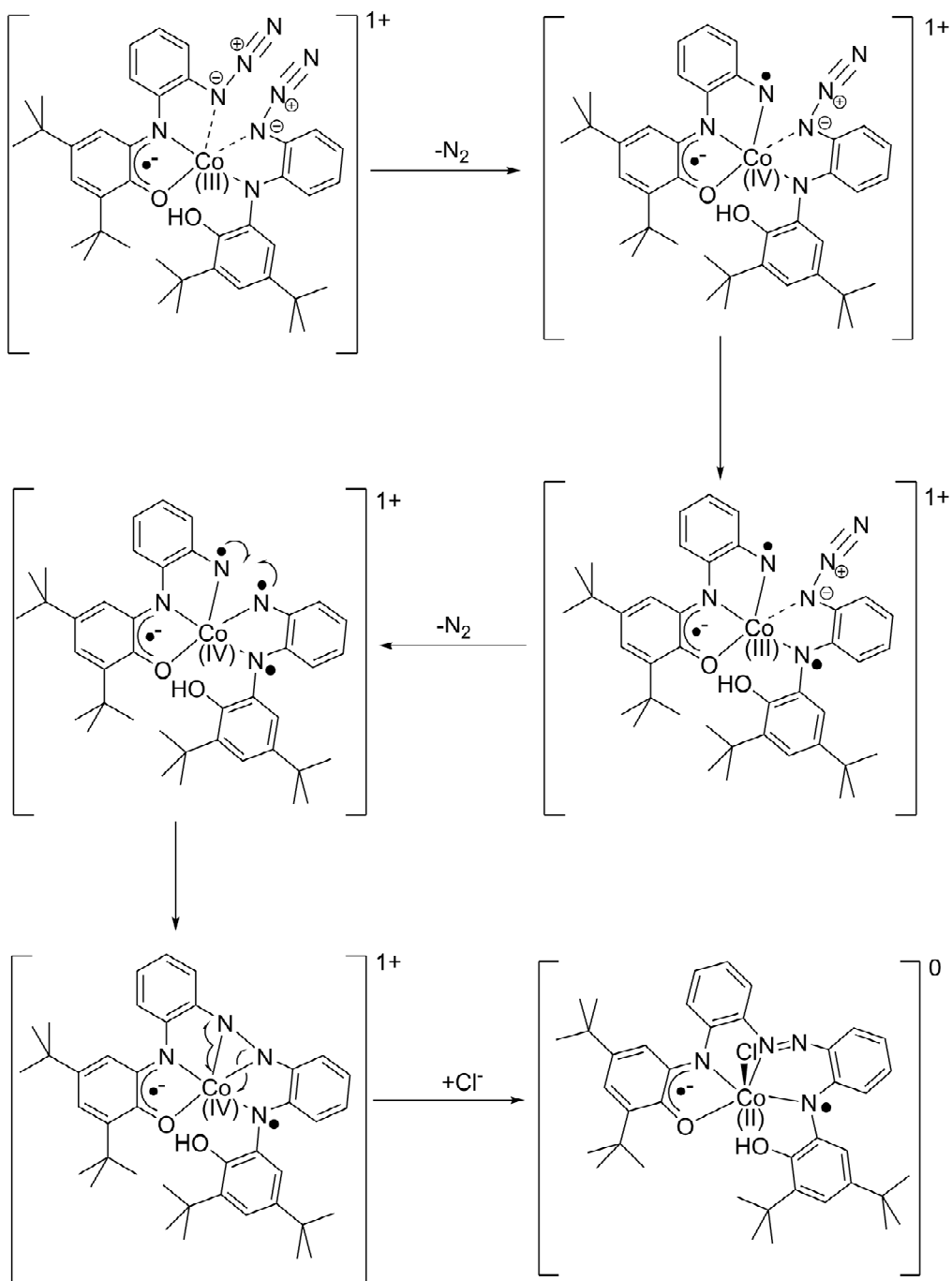
Table 3. Comparison of optimized bond distances (Å) (some selected ones) with those found by X-ray crystallographic measurement for **1**.

Bond Distance	X-ray crystal structure	Calculated
N2–N3	1.282(3)	1.28
N2–C12	1.434(4)	1.40
N4–C18	1.361(4)	1.34
N1–C1	1.355(4)	1.33
N1–C7	1.401(4)	1.38
N3–C13	1.365(4)	1.34
O1–C2	1.302(3)	1.27

Table 4. Parameters for the optimized geometry of **1**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	27	0	0.449281	1.332322	-0.109784
2	17	0	0.380507	1.545486	-2.421072
3	8	0	0.545159	-0.609844	-0.199039
4	7	0	0.738238	3.144721	0.245527
5	7	0	-1.406761	1.471321	0.236817
6	7	0	2.317434	1.172194	0.036228
7	8	0	-2.541828	0.374875	-2.102250
8	7	0	-0.076354	4.116862	0.418236
9	6	0	-1.403336	3.912032	0.427197
10	6	0	2.097537	3.487052	0.188940
11	6	0	2.978414	2.385781	0.041434
12	6	0	1.737931	-1.050974	-0.169756
13	6	0	-2.080288	2.628523	0.347626
14	6	0	-2.185436	0.270820	0.269816
15	6	0	-2.417663	-0.348419	1.494519
16	1	0	-1.944641	0.084665	2.372222
17	6	0	2.803229	-0.073921	0.064492
18	6	0	4.349964	2.636112	-0.155280
19	1	0	5.029624	1.826197	-0.383474
20	6	0	2.587106	4.795503	0.227858
21	1	0	1.887259	5.613642	0.349847
22	6	0	4.434437	-1.845357	0.251030
23	6	0	-3.510502	2.673024	0.439747
24	1	0	-4.055317	1.738319	0.391865
25	6	0	-3.265273	-1.452907	1.598574
26	6	0	-2.160433	5.112855	0.579012
27	1	0	-1.590982	6.035512	0.636380
28	6	0	1.037642	-3.466096	-0.793136
29	6	0	5.826995	-2.398815	0.558991
30	6	0	2.088600	-2.442659	-0.363050
31	6	0	3.401960	-2.769745	-0.139346
32	1	0	3.692665	-3.808571	-0.246436
33	6	0	-2.766586	-0.226985	-0.912649
34	6	0	4.130188	-0.509923	0.329209
35	1	0	4.873499	0.205896	0.648816
36	6	0	-3.524552	5.101062	0.643501
37	1	0	-4.087395	6.023202	0.749871
38	6	0	4.824705	3.938108	-0.125939
39	1	0	5.882835	4.124226	-0.286163
40	6	0	3.949517	5.013225	0.086310
41	1	0	4.336413	6.028176	0.112110
42	6	0	-3.867650	-1.901915	0.416685
43	1	0	-4.542133	-2.746155	0.474517
44	6	0	1.642446	-4.867100	-0.960585
45	1	0	2.434215	-4.887974	-1.719374
46	1	0	0.857772	-5.557495	-1.288941
47	1	0	2.049138	-5.259023	-0.019996
48	6	0	-3.374755	-2.302028	-3.160433
49	1	0	-3.908690	-2.648758	-4.054717
50	1	0	-2.773955	-3.137503	-2.782727
51	1	0	-2.700747	-1.494502	-3.451659
52	6	0	-3.653730	-1.324777	-0.841682
53	6	0	-4.194582	3.852920	0.572571

54	1	0	-5.280456	3.825710	0.624796
55	6	0	-4.386681	-1.837289	-2.094123
56	6	0	6.815604	-1.298057	0.963903
57	1	0	6.489802	-0.768395	1.866791
58	1	0	6.960141	-0.563853	0.162411
59	1	0	7.793116	-1.743440	1.179531
60	6	0	-5.271027	-0.711826	-2.671542
61	1	0	-6.024791	-0.397406	-1.939047
62	1	0	-5.799285	-1.072005	-3.563718
63	1	0	-4.677460	0.160132	-2.954284
64	6	0	-3.542647	-2.080210	2.972212
65	6	0	0.451829	-3.034307	-2.153391
66	1	0	-0.026310	-2.054333	-2.096833
67	1	0	-0.299514	-3.763488	-2.478679
68	1	0	1.235002	-2.993064	-2.919690
69	6	0	6.383198	-3.107370	-0.693719
70	1	0	7.381289	-3.510350	-0.483474
71	1	0	6.467880	-2.409287	-1.534229
72	1	0	5.752102	-3.942951	-1.014343
73	6	0	-0.084146	-3.554069	0.260520
74	1	0	0.319671	-3.866498	1.231653
75	1	0	-0.823751	-4.300835	-0.052698
76	1	0	-0.597351	-2.599115	0.385888
77	6	0	-5.304740	-3.028899	-1.781741
78	1	0	-6.090838	-2.770409	-1.062171
79	1	0	-4.747698	-3.889167	-1.391171
80	1	0	-5.799346	-3.350905	-2.705588
81	6	0	5.728030	-3.408188	1.721511
82	1	0	6.718072	-3.824944	1.942531
83	1	0	5.061366	-4.245046	1.487658
84	1	0	5.352376	-2.923823	2.630033
85	6	0	-2.218838	-2.515641	3.628933
86	1	0	-1.711741	-3.273776	3.021879
87	1	0	-2.407231	-2.943122	4.622128
88	1	0	-1.530103	-1.673200	3.754537
89	6	0	-4.234475	-1.038379	3.874207
90	1	0	-3.612874	-0.146597	4.010783
91	1	0	-4.437030	-1.461195	4.866700
92	1	0	-5.188301	-0.717054	3.439796
93	6	0	-4.454519	-3.311610	2.879422
94	1	0	-5.441390	-3.060608	2.473534
95	1	0	-4.608439	-3.732076	3.880348
96	1	0	-4.015599	-4.097276	2.253250
97	1	0	-1.689469	0.869340	-2.096502



Scheme 1. A mechanistic proposal is shown for the formation of **1**.

Reference:

- 1) M. Shen, T. G. Driver, *Org. Lett.*, 2008, **15**, 3367.