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Supporting information for article:

Variable temperature structural studies on valence tautomerism in cobalt bis(dioxolene) molecular complexes

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Table S1 Data collection and structure refinement details of **1S**

Temperature	296 K	200 K	175 K	150 K	100 K
CCDC Number	1450453	1450452	1450451	1450450	1450449
Empirical Formula	<chem>C38H46CoN2O4Br4.1.33C7H8</chem>				
M (gmol ⁻¹)	1065.47				
Crystal size (mm)	0.25*0.20*0.16				
Crystal system	Trigonal				
Space Group	P-3				
Crystallization	Toluene				
Solvent					
Temperature (K)	296	200	175	150	100
Radiation source	Bruker, Kappa Apex II				
λ, Å	0.56086				
a, Å	20.688(3)	20.4697(14)	20.3624(10)	20.255(2)	20.1281(7)
c, Å	9.0563(15)	9.0166(6)	9.0045(5)	9.0132(10)	8.9942(3)
V, Å ³	3356.6(12)	3271.9(5)	3233.3(4)	3202.3(8)	3155.7(2)
Z	3				
F(000)	1461				
ρ, g cm ⁻³	1.445	1.482	1.500	1.514	1.537
μ, mm ⁻¹	2.134	2.188	2.215	2.237	2.270
T _{max} , T _{min}	0.726, 0.618	0.721, 0.611	0.718, 0.607	0.716, 0.605	0.713, 0.601
Absorption correction	Multi-scan				
R _{int}	0.1350	0.1100	0.0920	0.1018	0.0852
Refinement method	Full-matrix least-squares on F ²				
N _{meas} , N _{uniq}	28207, 4605	11725, 4475	33637, 6344	13671, 4371	23579, 6428

Completeness	0.998	0.999	0.995	0.991	0.999
N _{obs} , N _{var}	2101, 229	2029, 229	3377, 229	2538, 229	3675, 223
R(F ²), wR(F ²) (I>2σ(I))	0.0745, 0.2007	0.0707, 0.1727	0.0726, 0.1862	0.0702, 0.1674	0.0572, 0.1359
Goodness of fit	1.000	0.889	1.049	1.005	0.993
Δρ _{min/max} eÅ ⁻³	-0.83/0.70	-0.81/0.67	-1.22/0.72	-1.21/0.81	-0.90/0.93

Table S2 Data collection and structure refinement details of **2S**

Temperature	296 K	200 K	175 K	150 K	100 K
CCDC Number	1450464	1450463	1450462	1450461	1450460
Empirical Formula			C ₃₈ H ₄₆ CoN ₂ O ₄ Cl ₄ .C ₇ H ₈		
M (gmol ⁻¹)			887.66		
Crystal size (mm)			0.18*0.16*0.10		
Crystal system			Trigonal		
Space Group			P-3		
Crystallization			Toluene		
Solvent					
Temperature (K)	296	200	175	150	100
Radiation source			Bruker, Kappa Apex II		
λ, Å			0.56086		
a, Å	20.643(18)	20.334(5)	20.243(5)	20.166(3)	20.0094(13)
c, Å	9.015(7)	8.945(5)	8.933(5)	8.9271(10)	8.8987(7)
V, Å ³	3327.0(6)	3203.0(2)	3170.0(2)	3143.9(9)	3085.5(5)
Z			3		
F(000)			1245		
ρ, g cm ⁻³	1.191	1.237	1.250	1.261	1.284
μ, mm ⁻¹	0.346	0.360	0.364	0.367	0.374

T _{max} , T _{min}	0.966, 0.940	0.965, 0.938	0.965, 0.937	0.964, 0.937	0.964, 0.936
Absorption correction	Multi-scan				
R _{int}	0.1544	0.1423	0.1296	0.1082	0.1417
Refinement method	Full-matrix least-squares on F ²				
N _{meas} , N _{uniqu}	11261, 4870	26508, 4414	13452, 4286	9956, 4641	25871, 4265
Completeness	0.983	0.994	0.986	0.987	0.996
N _{obs} , N _{var}	1440, 230	2591, 229	2085, 230	2214, 229	2901, 229
R(F ²), wR(F ²) (I>2σ(I))	0.1195, 0.2940	0.0930, 0.2479	0.1051, 0.2779	0.1063, 0.2802	0.0951, 0.2400
Goodness of fit	0.869	1.033	1.063	1.037	1.084
Δρ _{min/max} eÅ ⁻³	-0.45/0.65	-0.68/0.51	-0.50/0.64	-0.93/0.67	-0.87/0.99

Table S3 Data collection and structure refinement details of **1**

Temperature	296 K	250 K	235 K	200 K
CCDC Number	1450459	1450458	1450457	1450456
Empirical Formula	C ₃₈ H ₄₆ CoN ₂ O ₄ Br ₄			
M (gmol ⁻¹)	973.34			
Crystal size (mm)	0.20*0.17*0.14			
Crystal system	Triclinic			
Space Group	P-1			
Crystallization Solvent	Toluene			
Temperature (K)	296	250	235	200
Radiation source	Bruker, Kappa Apex II			
λ, Å	0.56086			
a, Å	9.0080(18)	8.9569(9)	9.0047(11)	8.9788(11)
b, Å	10.899(2)	10.7763(10)	10.2138(12)	10.1598(13)
c, Å	11.769(2)	11.7042(12)	11.6756(14)	11.6606(15)

α , °	85.328(6)	85.308(4)	86.394(4)	86.014(5)
β , °	87.483(6)	87.784(4)	89.775(5)	89.423(5)
γ , °	62.462(5)	62.483(3)	65.652(4)	65.463(4)
V, Å ³	1021.2(4)	998.56(17)	976.1(2)	965.1(2)
Z			1	
F(000)			487	
ρ , g cm ⁻³	1.583	1.619	1.656	1.675
μ , mm ⁻¹	2.338	2.391	2.446	2.474
T _{max} , T _{min}	0.735, 0.652	0.731, 0.646	0.726, 0.640	0.723, 0.637
Absorption correction			Multi-scan	
R _{int}	0.0760	0.0484	0.0493	0.0512
Refinement method			Full-matrix least-squares on F ²	
N _{meas} , N _{uniq}	10682, 4343	19168, 3924	18550, 3840	12572, 3104
Completeness	0.989	0.962	0.964	0.912
N _{obs} , N _{var}	2492, 229	2714, 229	2784, 229	2330, 229
R(F ²), wR(F ²) (I>2σ(I))	0.0606, 0.1463	0.0448, 0.1238	0.0455, 0.1182	0.0436, 0.1183
Goodness of fit	0.987	1.111	1.135	1.112
Δρ _{min/max} eÅ ⁻³	-0.66/1.38	-0.93/0.91	-0.99/1.26	-0.98/0.86

Table S3. Continued

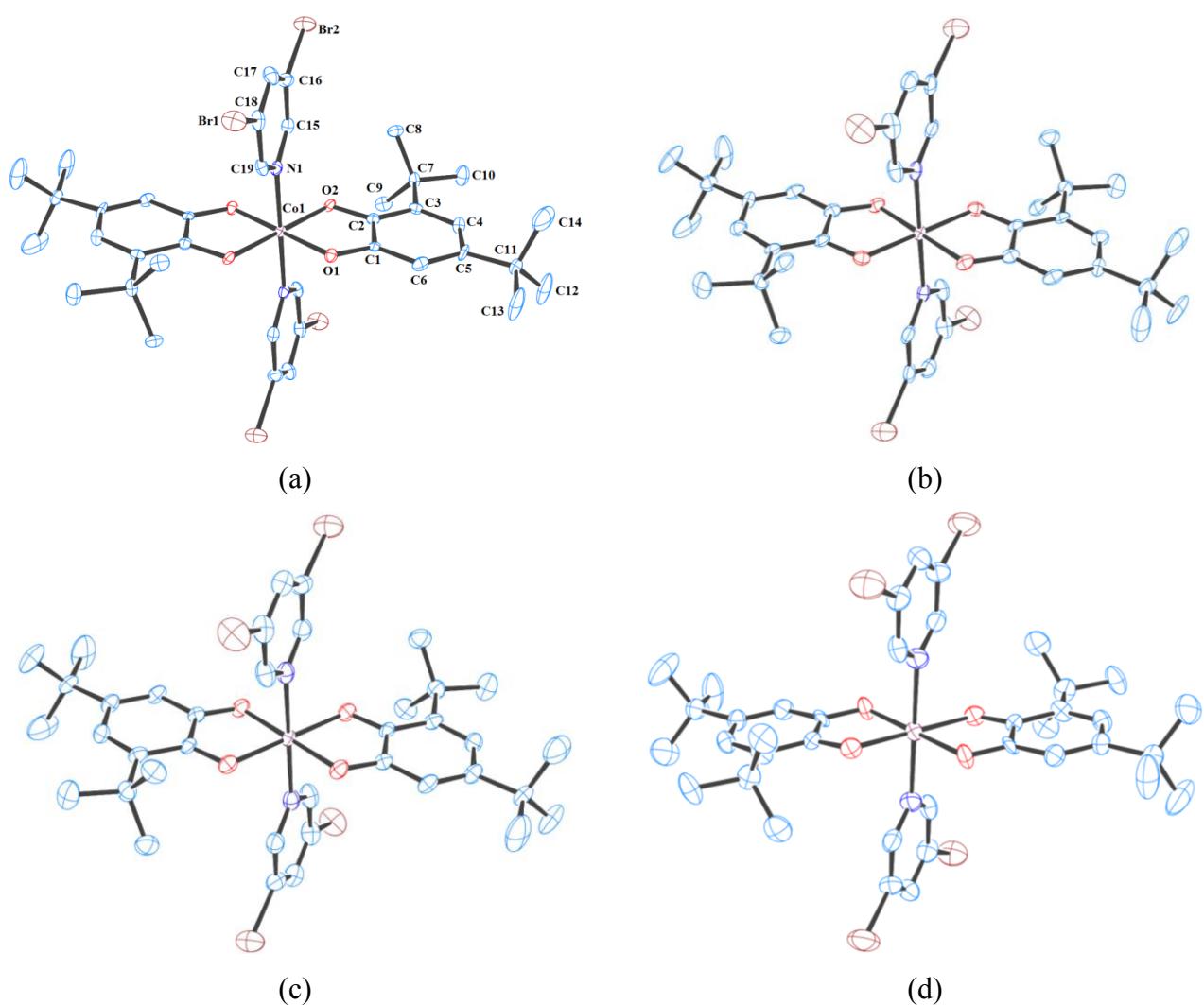
Compound	150 K	100 K
CCDC Number	1450455	1450454
Empirical Formula		C ₃₈ H ₄₆ CoN ₂ O ₄ Br ₄
M (gmol ⁻¹)		973.34
Crystal size (mm)		0.20*0.17*0.14
Crystal system		Triclinic
Space Group		P-1

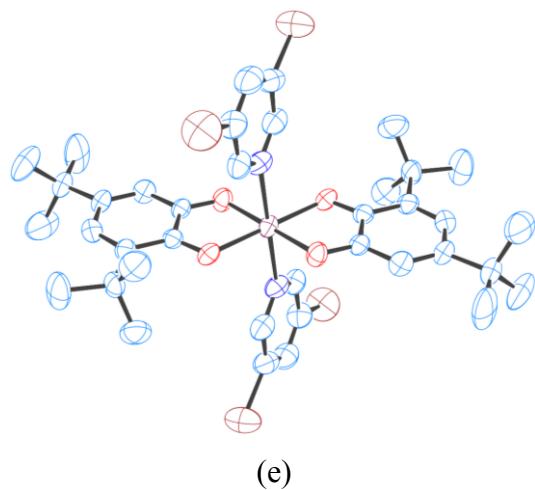
Crystallization Solvent	Toluene	
Temperature (K)	150	100
Radiation source	Bruker, Kappa Apex II	
λ , Å	0.56086	
a, Å	8.9612(7)	8.9545(6)
b, Å	10.1111(8)	10.1012(6)
c, Å	11.5984(9)	11.5659(8)
α , °	85.951(5)	85.879(3)
β , °	89.290(3)	89.310(4)
γ , °	65.221(4)	65.160(3)
V, Å ³	951.59(13)	946.72(11)
Z		1
F(000)		487
ρ , g cm ⁻³	1.698	1.707
μ , mm ⁻¹	2.509	2.522
T _{max} , T _{min}	0.720, 0.634	0.719, 0.632
Absorption correction	Multi-scan	
R _{int}	0.0442	0.0531
Refinement method	Full-matrix least-squares on F ²	
N _{meas} , N _{uniq}	17278, 3411	22010, 3770
Completeness	0.943	0.968
N _{obs} , N _{var}	2731, 229	3122, 229
R(F ²), wR(F ²) (I>2σ(I))	0.0354, 0.0947	0.0417, 0.1105
Goodness of fit	1.159	1.097
Δρ _{min/max} eÅ ⁻³	-0.82/1.33	-1.05/1.94

Table S4 Data collection and structure refinement details of **3** and **4**

Temperature	3-296 K	3-100 K	3-20 K	4-100 K
CCDC Number	1450467	1450465	1450466	1450468
Empirical Formula		C ₃₈ H ₄₄ CoN ₂ O ₄ Br ₆		C ₃₈ H ₄₄ CoN ₂ O ₄ Cl ₆
M (gmol ⁻¹)		1131.08		864.38
Crystal size (mm)		0.21*0.18*0.10		0.23*0.20*0.16
Crystal system			Triclinic	
Space Group			P-1	
Crystallization Solvent			Toluene	
Temperature (K)	296	100	20	100
Radiation source	Supernova	Supernova	SPring-8, BL02B1	Supernova
λ, Å	0.71073	0.71073	0.4997	0.71073
a, Å	8.8725(3)	8.8113(3)	8.8070(6)	8.7762(3)
b, Å	10.7980(3)	10.7232(5)	10.6922(8)	10.5578(4)
c, Å	11.6965(4)	11.5220(5)	11.4658(13)	11.4878(5)
α, °	92.641(2)	91.925(4)	91.692(8)	91.565(3)
β, °	94.358(3)	93.441(3)	93.393(7)	93.882(2)
γ, °	93.791(2)	93.722(3)	93.903(6)	93.950(4)
V, Å ³	1113.43(6)	1083.64(8)	1074.69(16)	1058.92(7)
Z			1	
F(000)		555		447
ρ, g cm ⁻³	1.687	1.733	1.748	1.355
μ, mm ⁻¹	5.806	5.965	2.370	0.823
T _{max} , T _{min}	0.594, 0.375	0.587, 0.367	0.815, 0.781	0.880, 0.833
Absorption correction	Multi-scan	Multi-scan	Empirical	Multi-scan
R _{int}	0.0738	0.0743	0.0658	0.0655
Refinement method	Full-matrix least-squares on F ²			
N _{meas} , N _{uniqu}	46994, 4865	22375, 4258	10578, 4320	20609, 4162

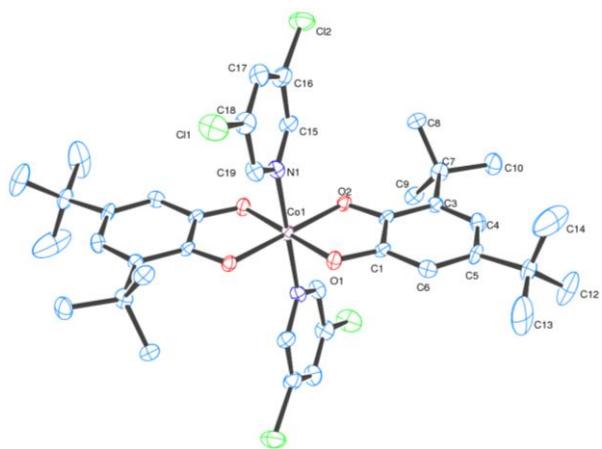
Completeness	0.993	0.978	0.989	1.000
$N_{\text{obs}}, N_{\text{var}}$	2879, 238	4258, 238	3504, 232	2864, 238
$R(F^2), wR(F^2) (I > 2\sigma(I))$	0.0445, 0.0862	0.0398, 0.0718	0.0600, 0.1517	0.0511, 0.1038
Goodness of fit	1.012	1.046	1.118	1.035
$\Delta\rho_{\text{min/max}} \text{ e}\text{\AA}^{-3}$	-0.34/0.40	-0.61/0.77	-2.09/1.81	-0.34/0.69



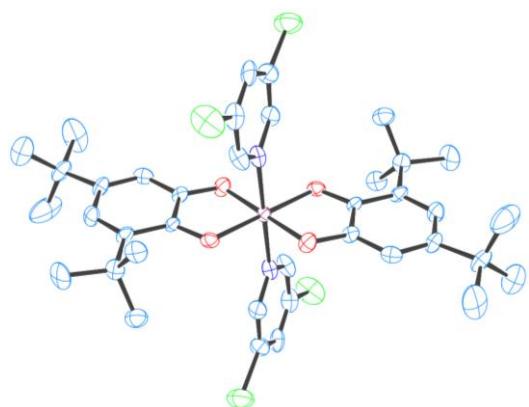


(e)

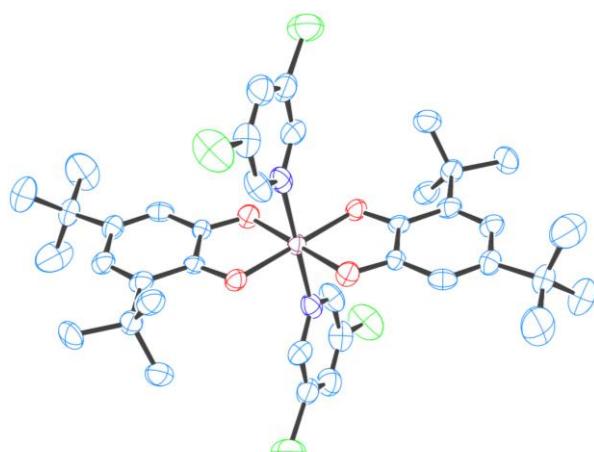
Figure S1. ORTEP drawing of **1S** showing 50% probability ellipsoids at (a) 100 K (b) 150 K (c) 175 K (d) 200 K and (e) 296 K. Atomic labels are shown for the asymmetric unit and the same atomic labelling was used for all figures. All hydrogen atoms were omitted for clarity.



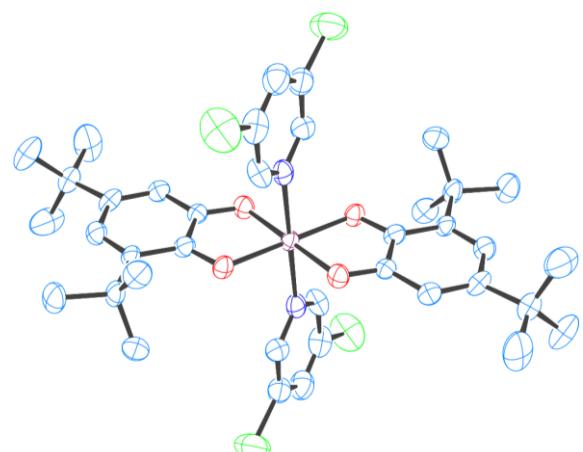
(a)



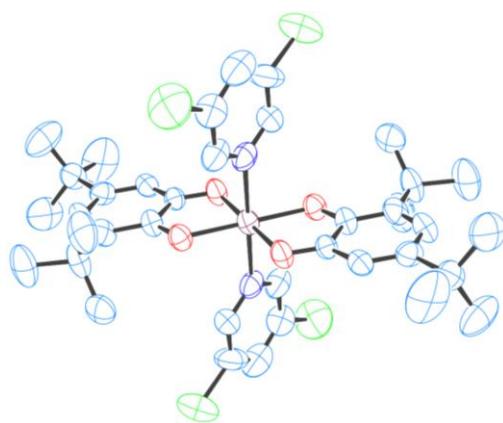
(b)



(c)

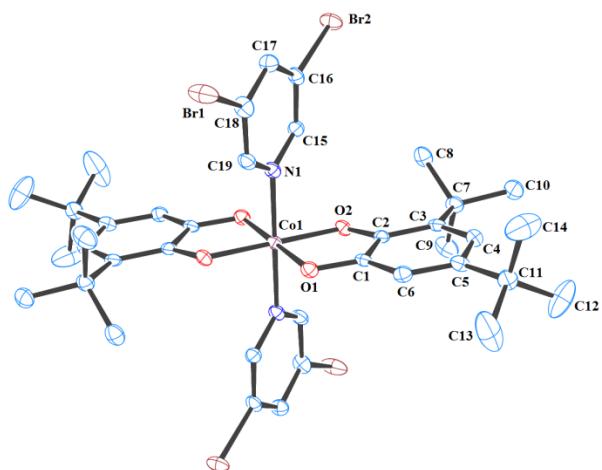


(d)

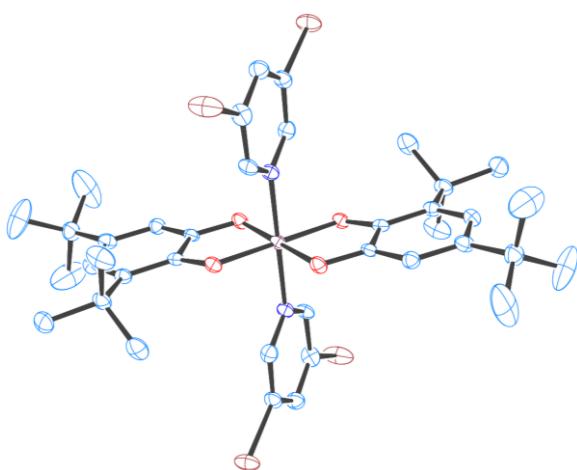


(e)

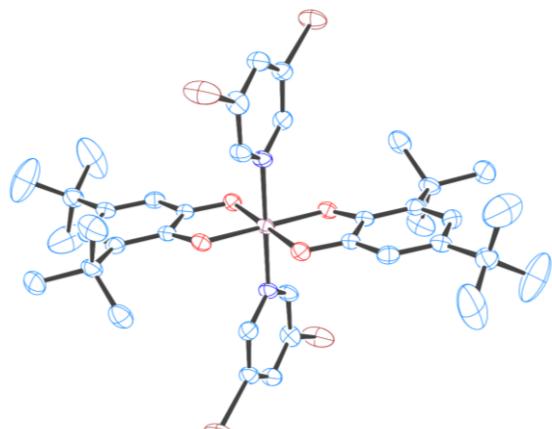
Figure S2. ORTEP drawing of **2S** showing 50% probability ellipsoids at (a) 100 K (b) 150 K (c) 175 K (d) 200 K and (e) 296 K. Atomic labels are shown for the asymmetric unit and the same atomic labelling was used for all figures. All hydrogen atoms were omitted for clarity.



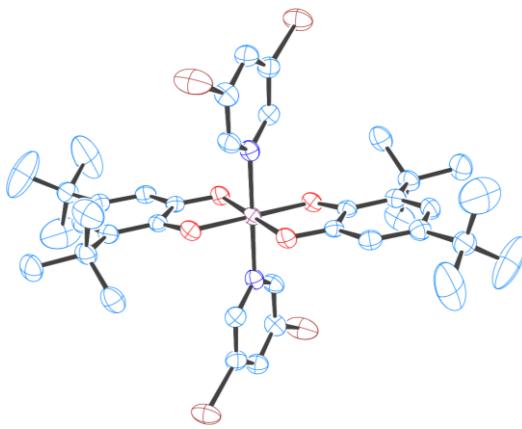
(a)



(b)



(c)



(d)

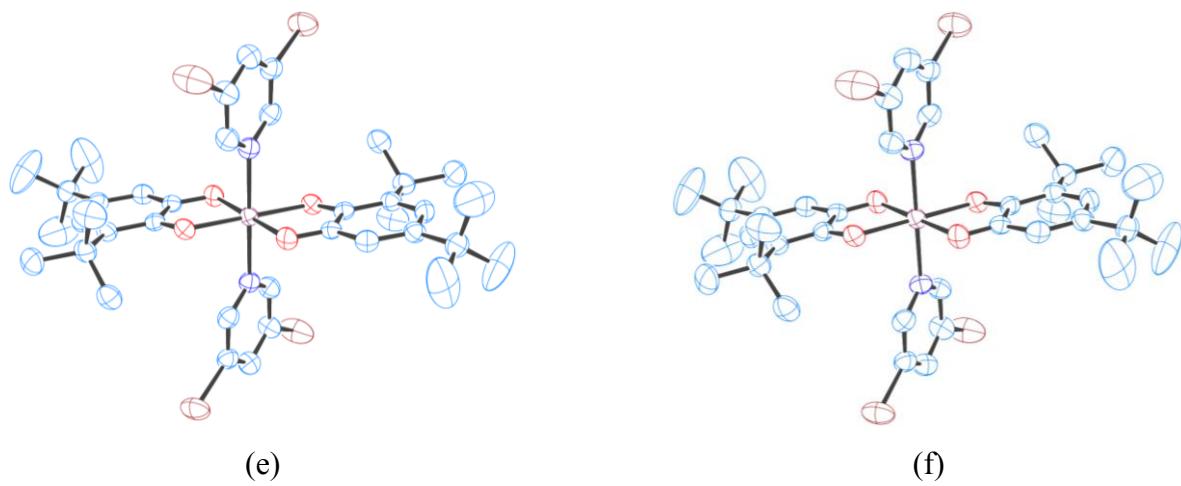
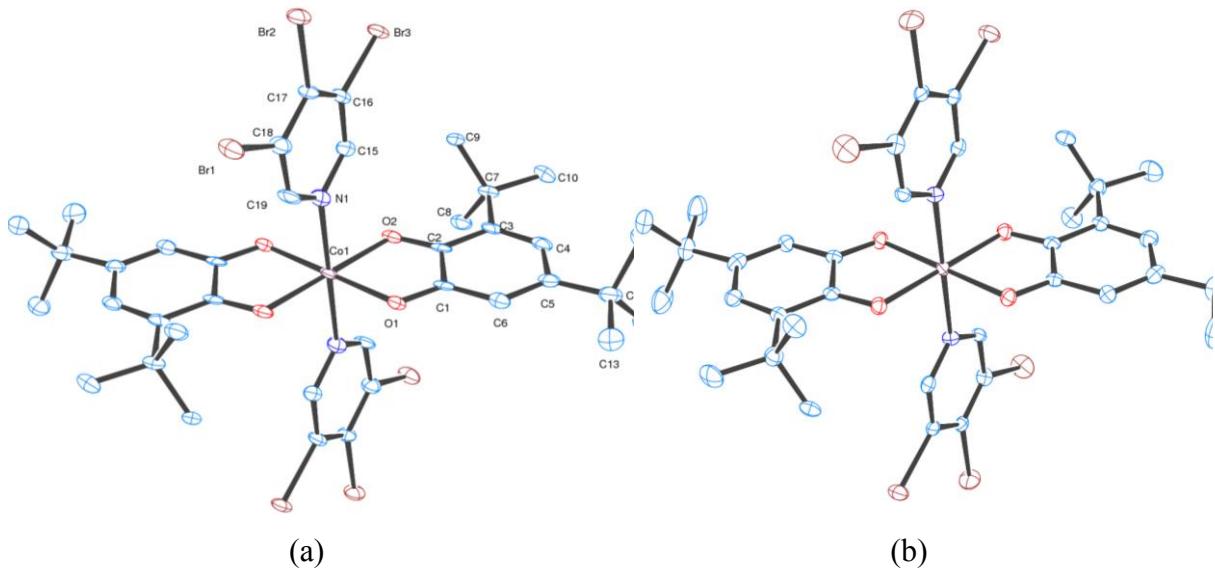


Figure S3. ORTEP drawing of **1** showing 50% probability ellipsoids at (a) 100 K (b) 150 K (c) 200 K (d) 235 K (e) 250 K and (f) 296 K. Atomic labels are shown for the asymmetric unit and the same atomic labelling was used for all figures. All hydrogen atoms were omitted for clarity.



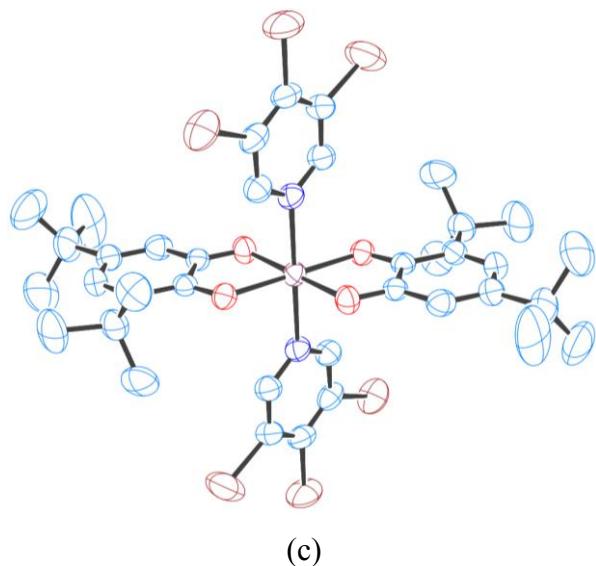


Figure S4. ORTEP drawing of **3** showing 50% probability ellipsoids at (a) 20 K (b) 100 K and (c) 296 K. Atomic labels are shown for the asymmetric unit and the same atomic labelling was used for all figures. All hydrogen atoms were omitted for clarity.

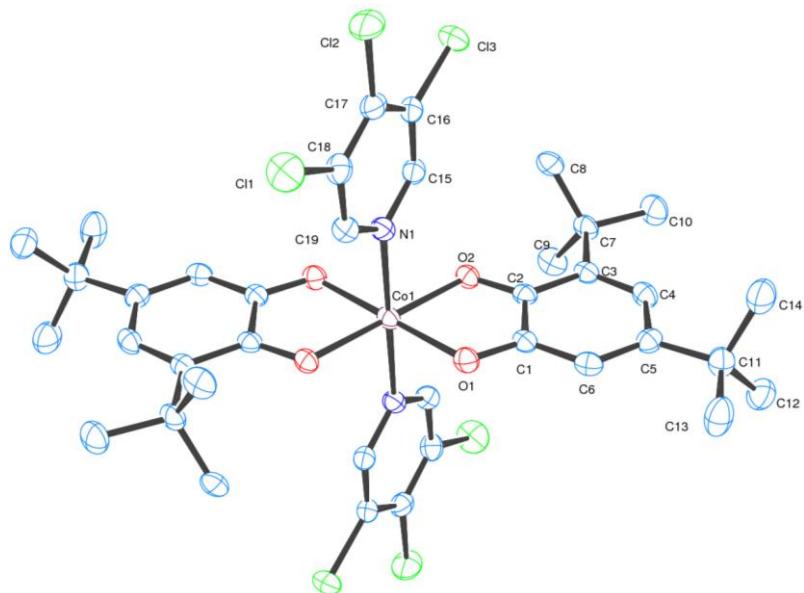


Figure S5. ORTEP drawing of **4** showing 50% probability ellipsoids at 100 K. Atomic labels are shown for the asymmetric unit and all hydrogen atoms were omitted for clarity.

Table S5 Selected bond lengths (\AA) after TLS corrections for **1S**, **1**, **2S**, **3** and **4** at different temperatures.

Compound	Bond	20 K	100 K	150K	175K	200K	235K	250K	296K
1S	Co-O1	-	1.891	1.936	1.987	2.011	-	-	2.039
	Co-O2	-	1.896	1.944	1.998	2.024	-	-	2.053
	Co-N1	-	1.976	2.039	2.108	2.162	-	-	2.211
	C1-O1	-	1.333	1.327	1.308	1.289	-	-	1.297
	C2-O2	-	1.344	1.337	1.308	1.289	-	-	1.285
1	Co-O1	-	1.884	1.886		1.894	1.899	2.015	2.042
	Co-O2	-	1.891	1.890	-	1.897	1.904	2.036	2.067
	Co-N1	-	1.945	1.948	-	1.955	1.972	2.145	2.183
	C1-O1	-	1.324	1.335	-	1.336	1.333	1.296	1.274
	C2-O2	-	1.329	1.332	-	1.340	1.331	1.285	1.286
2S	Co-O1	-	1.884	1.926	1.960	2.004	-	-	2.043
	Co-O2	-	1.890	1.924	1.956	2.000	-	-	2.044
	Co-N1	-	1.963	2.015	2.075	2.134	-	-	2.220
	C1-O1	-	1.319	1.328	1.318	1.284	-	-	1.257
	C2-O2	-	1.312	1.315	1.313	1.307	-	-	1.306
3	Co-O1	2.033	2.042	-	-	-	-	-	2.043
	Co-O2	2.032	2.054	-	-	-	-	-	2.061
	Co-N1	2.158	2.197	-	-	-	-	-	2.218
	C1-O1	1.283	1.286	-	-	-	-	-	1.278
	C2-O2	1.284	1.297	-	-	-	-	-	1.294
4	Co-O1	-	2.039	-	-	-	-	-	-
	Co-O2	-	2.047	-	-	-	-	-	-
	Co-N1	-	2.196	-	-	-	-	-	-
	C1-O1	-	1.286	-	-	-	-	-	-
	C2-O2	-	1.294	-	-	-	-	-	-

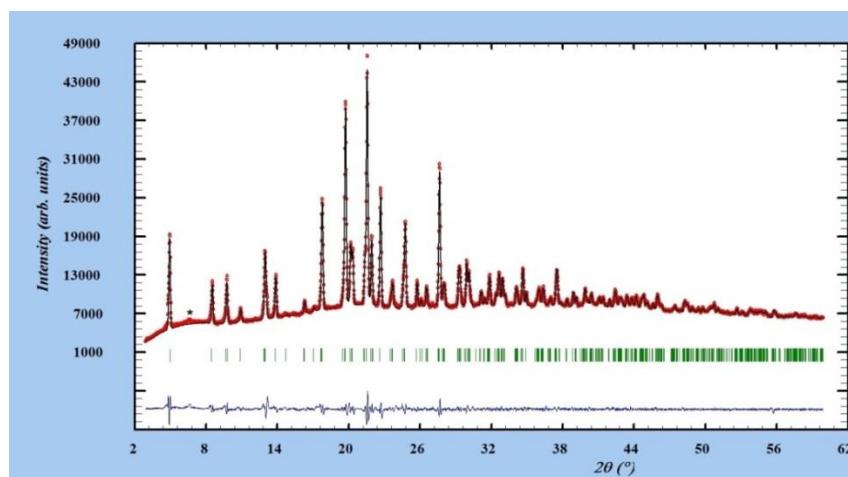


Figure S6. PXRD pattern of as synthesized sample of **1S**. A small quantity of impurity phase, $(\text{CoSQ}_2)_4$ is indicated by * in the pattern.

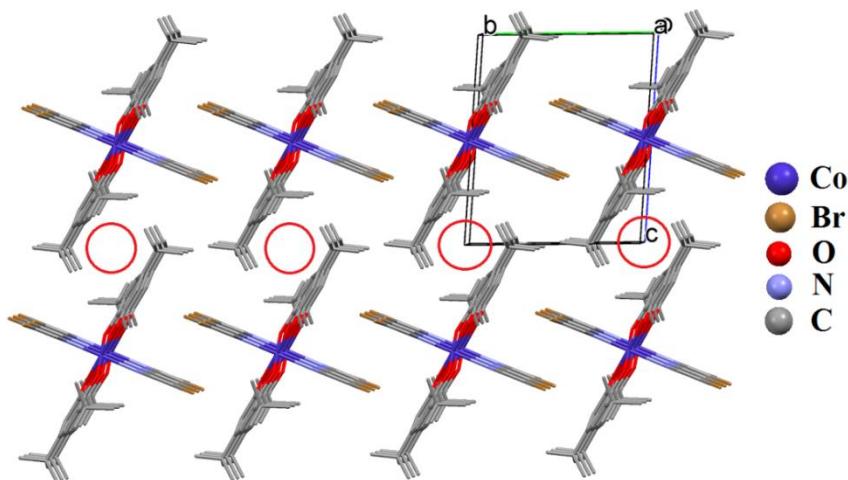


Figure S7. A demonstration of lattice solvent molecules (red circle) in the packing diagram of **1S**. Hydrogens are omitted for clarity.

S1. Vibrating sample magnetometry

Magnetic susceptibility measurements were carried out on a sample pellets using a Physical Properties Measurements System equipped with a MicroSense VSM EZ7 model vibrating-sample magnetometer. Data were collected in the temperature range of 2–300 K with an applied external magnetic field of 1 Tesla. All measured susceptibilities were corrected for the molecular diamagnetic contributions through Pascal's method.

S2. Variable temperature magnetic properties

The magnetic moments for samples **1S**, **2S**, **3** and **4** were measured during cooling and heating between 2 K and 300 K in a magnetic field of 1 Tesla. The molar magnetic susceptibility is plotted as χ_{MT} vs T in Figure S8 (where χ_M is the molar magnetic susceptibility and T is temperature). At 300 K, the χ_{MT} values are 3.43, 3.51, 3.68 and 3.54 cm³.K.mol⁻¹ for samples **1S**, **2S**, **3** and **4**, respectively. Two S=1/2 3,5-DBSQ-radicals and the hs-Co^{II} (S=3/2) will give an expected spin-only χ_{MT} value of 2.625 cm³.K.mol⁻¹, which is significantly lower than measured. However, the measured χ_{MT} values are similar to studied hs-Co^{II} complexes in the literature,(Schmidt, Shultz, Martin, *et al.*, 2010; Schmidt, Shultz & Martin, 2010; Chen *et al.*, 2014; Paquette *et al.*, 2009) likely resulting from significant orbital contribution to the susceptibility from the anisotropic Co^{II}-ion, and indicating that all samples are in a hs-(3,5-DBSQ)₂ oxidation state at room temperature.

For samples **1S** and **2S**, χ_{MT} values decrease slowly to ca. 3 cm³.K.mol⁻¹ while cooling the sample to 200 K. Upon further decreasing the temperature, both samples display a steeper decrease in χ_{MT} values which is due to VT conversion from hs-Co^{II}(3,5-DBSQ)₂ to ls-Co^{III}(3,5-DBSQ)(3,5-DBCat), where one electron is transferred from the e_g levels to t_{2g} levels of the Co ion and another electron is transferred to one of the two 3,5-DBSQ ligands. At 50 K, when the VT from the structural analysis is complete, χ_{MT} is 0.95 cm³.K.mol⁻¹ (expected spin only value is 0.38 cm³.K.mol⁻¹ as the only paramagnetic species is one DBSQ-radical) which again is due to unquenched orbital angular momentum. A similar trend in the magnetic data was previously observed for other cobalt VT complexes.(Cheng *et al.*, 2015; Slota *et al.*, 2015; Affronte *et al.*, 2007; Poneti *et al.*, 2013; Bodnar *et al.*, 2001; Liang *et al.*, 2007) The large decrease in the magnetic moments confirm the presence of thermal VT in samples **1S** and **2S**, as also deduced from the structural changes. When warming up from 2 K to 300 K, all samples regain their initial susceptibility indicating that the VT transition is thermally-reversible, and there is no sign of hysteresis for the measured magnetic moments in any sample.

For samples **3** and **4**, the χ_{MT} value changes from 3.68 to 3.01 cm³.K.mol⁻¹ and 3.54 to 2.90 cm³.K.mol⁻¹, respectively while cooling samples from room temperature to 2 K (Figure S8). Even though there is a slight decrease in χ_{MT} values, its value corresponds to the hs-Co^{II}(3,5-DBSQ)₂ oxidation state of VT complexes, which is consistent with literature values.(Schmidt, Shultz, Martin, *et al.*, 2010; Schmidt, Shultz & Martin, 2010; Chen *et al.*, 2014; Tao *et al.*, 2006) This type of magnetic behaviour has previously been observed for hs-Co^{II}(3,5-DBSQ)2(Py2O) VT complex during cooling,(Jung *et al.*, 1997) and strongly suggests that compounds **3** and **4** do not undergo any thermally driven VT conversion during cooling. The results from magnetic measurements are consistent with the changes in the Co-N/O bond distances observed in the variable temperature crystal structure analysis.

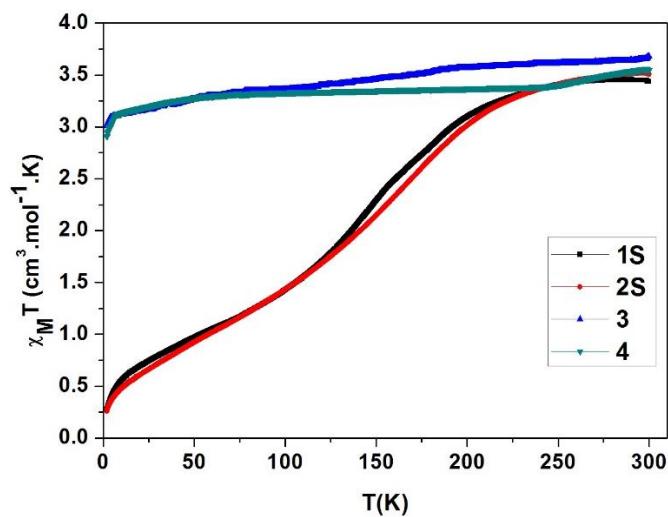


Figure S8. Variable temperature magnetic susceptibility plotted as $\chi_M T$ vs T for samples **1S**, **2S**, **3** and **4**.