Article

Triggering of Valence Tautomeric Transitions in Dioxolene-Based Cobalt Complexes Influenced by Ligand Substituents, Co-ligands, and Anions

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Electronic Supplementary Information

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S1. ^{1}H-NMR Spectra:

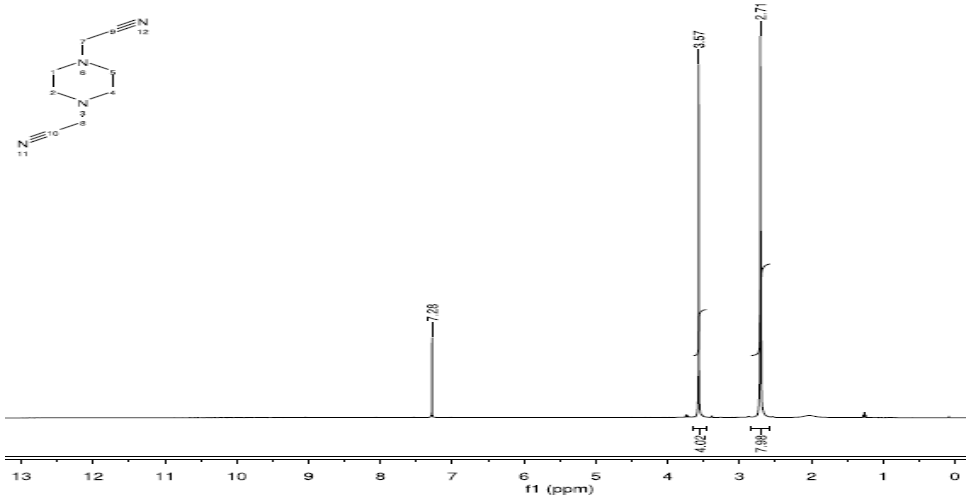

Figure S1. ^{1}H-NMR spectra of N,N′-Bis(cyanomethyl)piperazine.

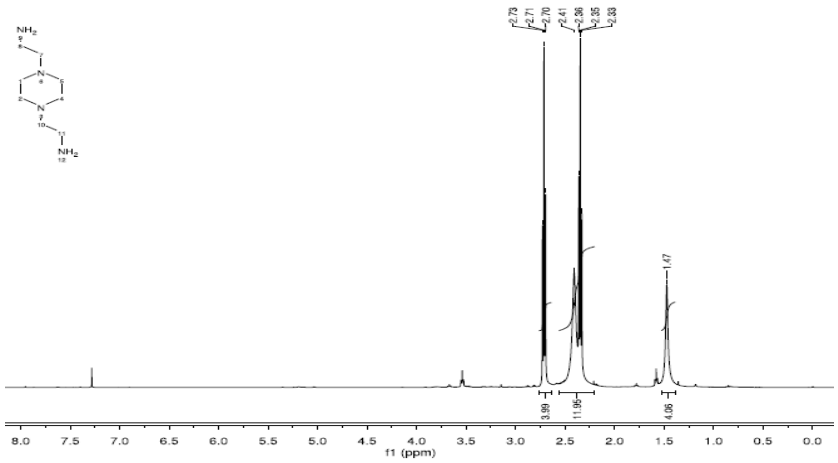

Figure S2. [1]H-NMR spectra of N,N′-Bis(2-aminoethyl)piperazine.

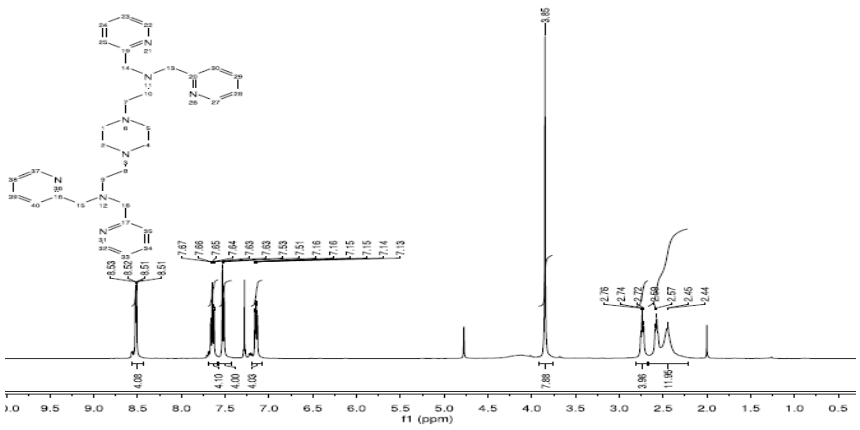

Figure S3. [1]H-NMRspectraof1,1′-(piperazine-1,4-diyl)bis(N,Nbis(pyridinylmethyl)methanamine)(**L^{tpbap}**) octadentate ligand.

S2. [13]C-NMR Spectra:

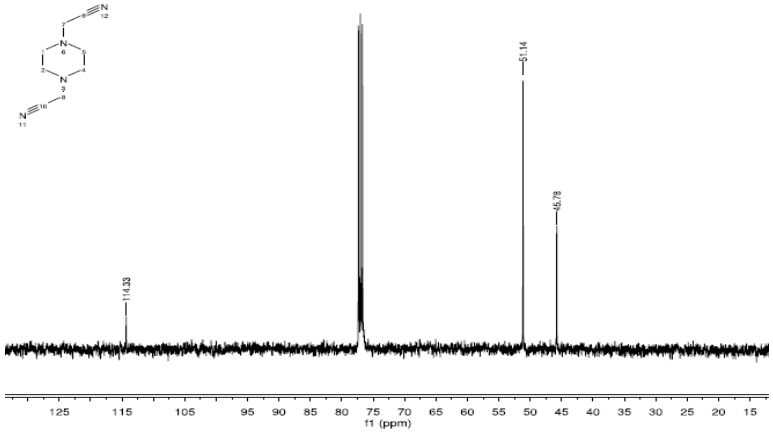

Figure S4. [13]C-NMR spectra of N,N′-Bis(cyanomethyl)piperazine.

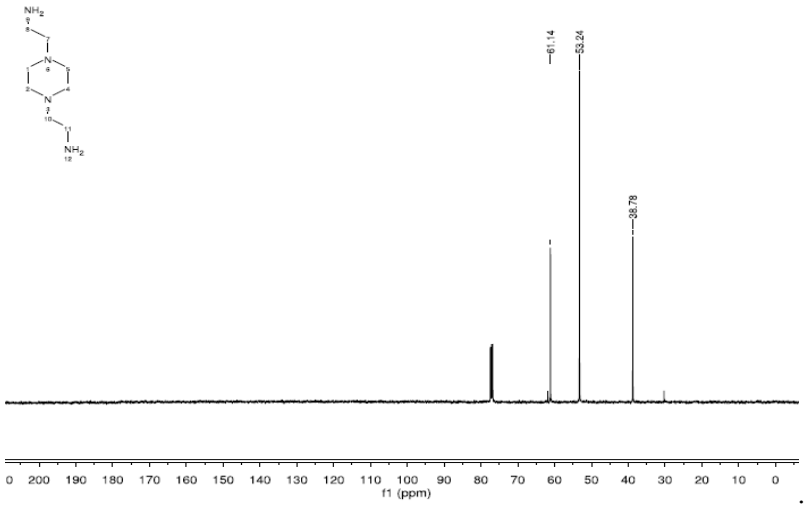

Figure S5. ^{13}C-NMR spectra of N,N′-Bis(2-aminoethyl)piperazine.

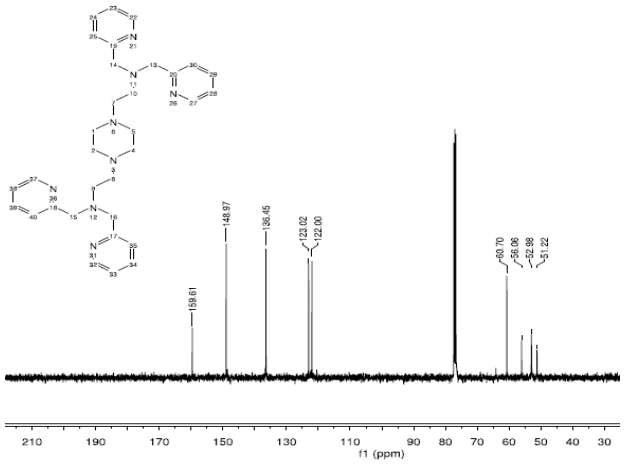

Figure S6. ^{13}C-NMR spectra of N,N,N′,N′-Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L^{tpbap}**).

S3 Infrared Spectra

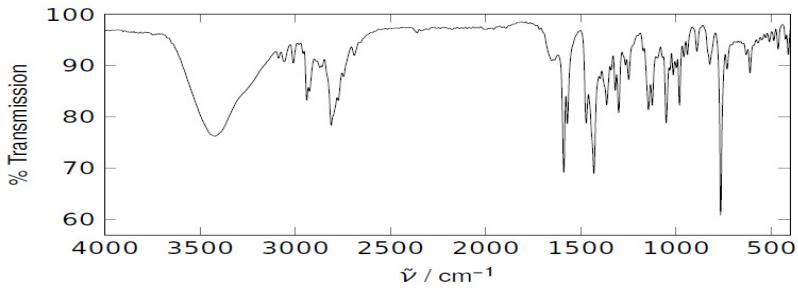

Figure S7. Infrared spectra of 1,1′-(piperazine-1,4-diyl)bis(N,Nbis(pyridinylmethyl)methanamine)(**L^{tpbap}**) octadentate ligand.

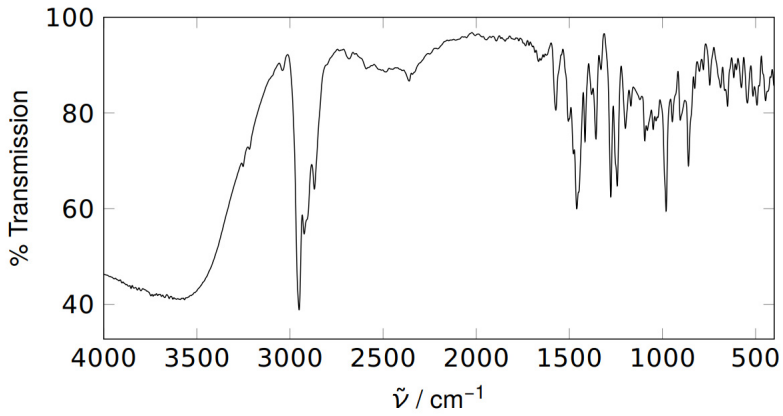

Figure S8. Infrared spectra of ligand [Co(**3,5-dbsq**)(**3,5-dbcat**)$_2$(4-Mepip)$_2$] (**1**).

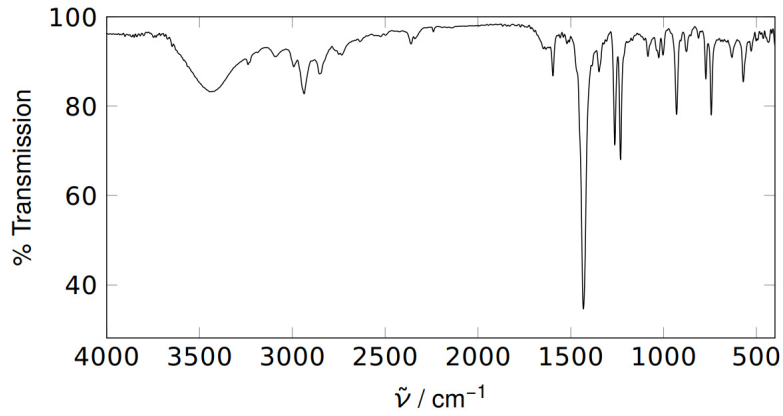

Figure S9. Infrared spectra of ligand [Co(**tbcat**)$_2$(pip)$_2$] CH_3CN (**2**).

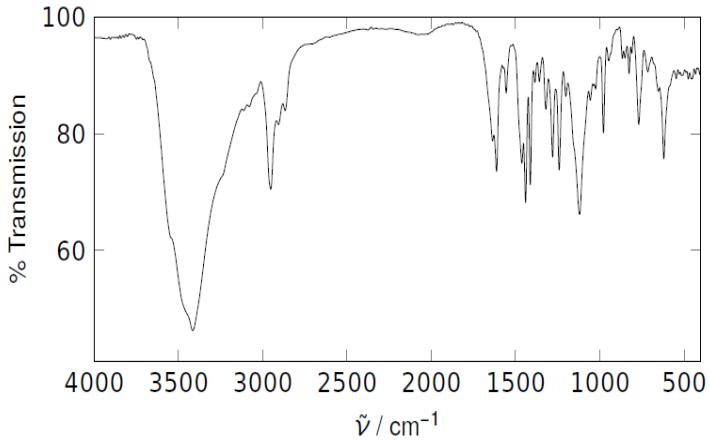

Figure S10. Infrared spectra of ligand [Co2(Ltpbap)(3,5-dbcat)2](SO4)·5.5MeOH·2H2O (3a).

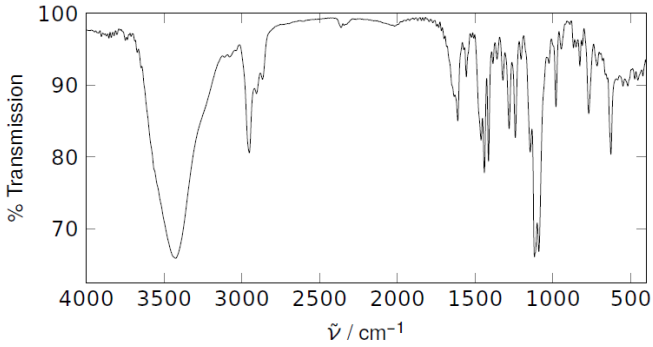

Figure S11. Infrared spectra of ligand [Co_2 (**L**^{tpbap})(**3,5-dbcat**)$_2$](ClO_4)2·1.5 H_2O (**3b**).

S4 Bond Length Tables and Crystal Structure at 173 K

Table S1. Selected bond length for complex 1 at 173 K.

Bond	Bond length (Å)
O1-C1	1.302(15)
O2-C2	1.312(14)
O3-C15	1.348(15)
O4-C16	1.362(14)
C1-C2	1.470(16)
C2-C3	1.393(16)
C3-C4	1.399(16)
C4-C5	1.413(15)
C5-C6	1.372(17)
C6-C1	1.409(19)
C15-C16	1.423(16)
C16-C17	1.404(15)
C17-C18	1.407(16)
C18-C19	1.391(15)
C19-C20	1.388(17)
C20-C15	1.369(19)

Table S2. Selected bond length for complex 2 at 173 K.

Bond	Bond length (Å)
O1-C1	1.333(5)
O2-C2	1.318(5)
O3-C7	1.334(5)
O4-C8	1.315(5)
C1-C2	1.445(6)
C2-C3	1.385(6)
C3-C4	1.413(6)
C4-C5	1.396(6)
C5-C6	1.394(6)
C6-C1	1.397(6)
C7-C8	1.417(6)
C8-C9	1.412(6)
C9-C10	1.403(7)
C10-C11	1.391(7)

C11-C12	1.410 (7)
C12-C7	1.378(6)

Table S3. Bond valence sum values (BVS) are calculated from literature known formula $z_j = \sum S_{ij}$ tabulated extracted and calculated from the X-ray data obtained at 173 K for the Co ions in complex **1**,**2**, **3a** and **3b**.

Complex	Oxidation state 2+ (HS)	Oxidation state 3+ (LS)
Complex **1**	3.2841	2.9287
Complex **2**	3.1199	2.7796
Complex **3a**	3.2307	2.9278
Complex **3b**	3.2407	2.9377

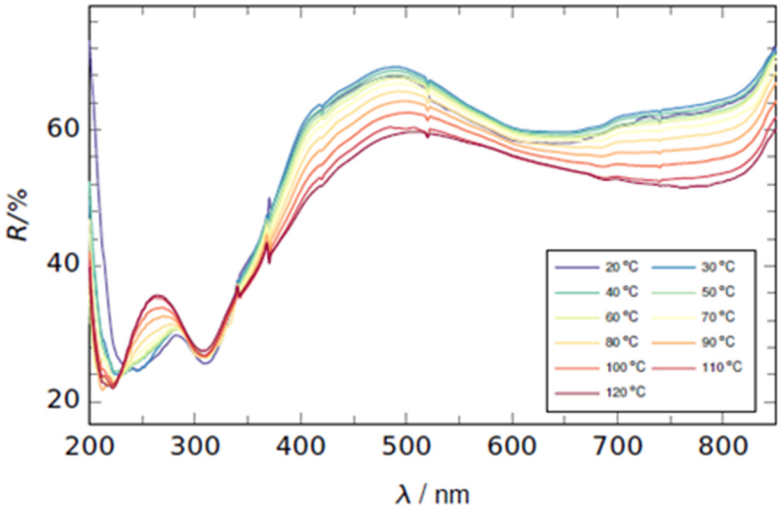

Figure S12. Solid state reflectance spectra for complex 1. The temperature dependence of the reflectance shows a VT- transition between 20 ˚C and 120 ˚C.

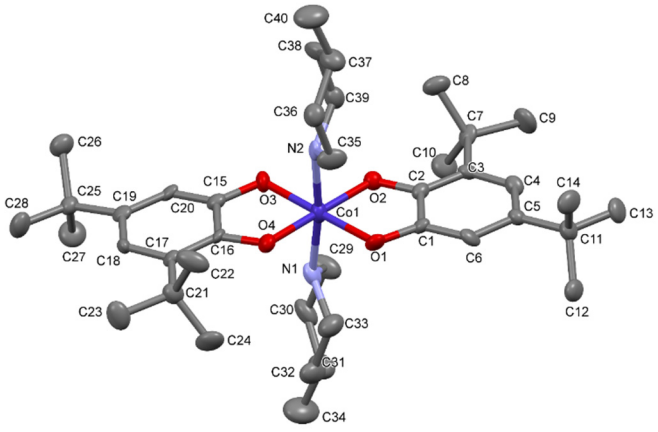

Figure S13. Complex structure of 1 at 173 K with atom labels. Thermaldisplacement probability set to 50%; hydrogen atoms are omitted for clarity.

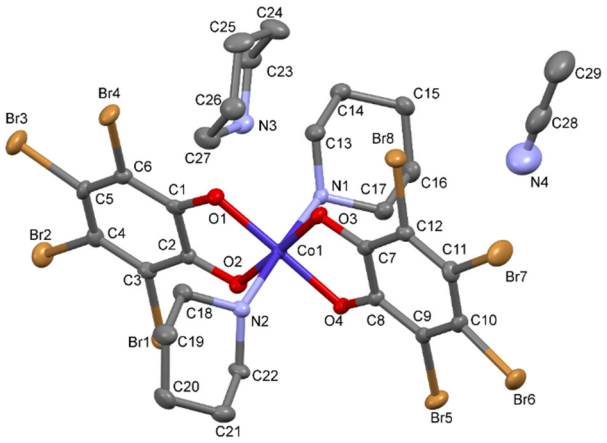

Figure S14: Complex structure of **2** at 173 K with atom labels. Thermal displacement probability set to 50%; hydrogen atoms are omitted for clarity.