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Supporting Information

Complete Direct and Reverse Optically Induced Valence Tautomeric Interconversion in a Cobalt-Dioxolene Complex

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Experimental section

Synthesis

Me_2tpa ligand was synthesised according to literature methods.[17,18] The complexes were obtained mixing methanol solutions containing cobalt chloride and the ligand in 1:1 ratio with a solution of the catecholate and triethylamine (1:2.5 ratio) in the same solvent under inert atmosphere. The metal(II)-catecholato complexes were oxidised with atmospheric dioxygen and the resulting products were precipitated by adding an aqueous solution of KPF_6.

Photomagnetic characterization

The photomagnetic characterization of the sample was performed by irradiating thin pellets (1–2 mg) of polycrystalline powder. The experiments were performed by a S600 Cryogenic SQUID Magnetometer equipped with an optical fiber and a specifically designed sample holder. Earlier calibration of the setup was accomplished to remove any stray contributions due to the arrangement. The data have been recorded exciting the sample at 9 K until the steady state was reached, then raising the temperature and letting it stabilise for 300 s. This is the time zero in the relaxation measurements. The relaxation data have been recorded exciting the sample at 9 K until the steady state was reached (10 hours), then raising the temperature to desired value and letting it stabilise for 300 s. This is the time zero of the relaxation measurements.

Diffractometric analysis

X-ray data collection for **1** was performed on an Oxford Instrument XcaliburPX Ultra diffractometer equipped with a 165 mm CCD area detector and using graphite monochromated CuK_α radiation from the Enhance high-brilliance sealed tube. The diffraction data were collected at 100 and 160 K using an Oxford Cryostream liquid-nitrogen cooling system. Details of the unit cell and the partial refinement results are reported in Tables S1 and S2; selected parameters at the two temperatures are given in Tables S3.

Table S1. Crystal data and structure refinement for **1** at 100 K

Empirical formula	C82 H100 Co2 F12 N8 O4 P2	
Formula weight	1669.5	
Temperature	100(2) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.475(5) Å	α= 90°.
	b = 31.009(5) Å	β= 94.458(5)°.
	c = 21.784(5) Å	γ = 90°.
Volume	7728(4) Å^3	
Z	4	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	4.481 mm^{-1}	
F(000)	3488	
Crystal size	0.21 x 0.14 x 0.05 mm^3	
Theta range for data collection	3.86 to 54.3°.	
Index ranges	-12=h=12, -32=k=29, -22=l=22	
Reflections collected	28930	
Independent reflections	9314 [R(int) = 0.1036]	
Completeness to theta = 54.3°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9 and 0.36	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9314 / 11 / 890	
Goodness-of-fit on F^2	1.888	
Final R indices [I>2sigma(I)]	R1 = 0.1846, wR2 = 0.4846	
R indices (all data)	R1 = 0.2592, wR2 = 0.529	
Largest diff. peak and hole	1.885 and -0.793 e.Å^{-3}	

Table S2 Crystal data and structure refinement for **1** at 160 K

Empirical formula	C82 H100 Co2 F12 N8 O4 P2	
Formula weight	1669.5	
Temperature	160(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.559(5) Å	α= 90.000(5)°.
	b = 31.395(5) Å	β= 94.837(5)°.
	c = 21.918(5) Å	γ = 90.000(5)°.
Volume	7926(4) Å^3	
Z	4	
Density (calculated)	1.399 Mg/m^3	
Absorption coefficient	4.37 mm^{-1}	
F(000)	3488	
Crystal size	0.21 x 0.14 x 0.05 mm^3	
Theta range for data collection	1.77 to 21.91°.	
Index ranges	-12=h=12, -32=k=29, -23=l=22	
Reflections collected	30621	
Independent reflections	9464 [R(int) = 0.0913]	
Completeness to theta = 21.91°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.991 and 0.8874	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9464 / 7 / 921	
Goodness-of-fit on F^2	2.137	
Final R indices [I>2sigma(I)]	R1 = 0.1957, wR2 = 0.5230	
R indices (all data)	R1 = 0.2593, wR2 = 0.5605	
Largest diff. peak and hole	2.136 and -0.619 e.Å^{-3}	

Table S3 Selected bond distances (Å) for **1** at 100 K and 160 K

100 K		**160 K**	
Co1-O1	1.873(11)	Co1-O1	1.987(13)
Co1-O2	1.893(12)	Co1-O2	2.050(12)
Co1-N1	1.988(13)	Co1-N1	2.099(13)
Co1-N3	2.013(15)	Co1-N2	2.126(15)
Co1-N2	2.028(15)	Co1-N3	2.142(17)
Co1-N4	2.042(16)	Co1-N4	2.168(16)
O1-C11	1.32(2)	O1-C11	1.33(2)
O2-C12	1.302(19)	O2-C12	1.28(2)
C11-C12	1.39(2)	C11-C12	1.49(2)
Co2-O4	1.870(11)	Co2-O3	1.879(12)
Co2-O3	1.880(11)	Co2-O4	1.879(13)
Co2-N5	1.961(14)	Co2-N7	1.991(14)
Co2-N7	2.000(14)	Co2-N5	1.995(15)
Co2-N8	2.007(15)	Co2-N8	2.020(16)
Co2-N6	2.034(16)	Co2-N6	2.041(15)
O3-C32	1.32(2)	O3-C32	1.34(2)
O4-C33	1.375(18)	O4-C33	1.351(19)
C32-C33	1.39(2)	C32-C33	1.41(2)