Supporting information to accompany

Solvation effects on the valence tautomeric transition of a cobalt complex in the solid state

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Fig. S1 A structural representation indicating the face-to-face intermolecular π - π stacking interactions in 1.0.5py *via* the pyridine molecules of type ligand...ligand (3.42 Å) and ligand...solvate (3.48 Å).



Fig. S2 Structural representation of complex 1 in 1.2MeCN (solvent molecules not shown).



Fig. S3 (a) Structural representation indicating the ligand…ligand intermolecular π - π stacking interaction (3.71 Å) in 1.2MeCN. (b) Crystal packing in 1.2MeCN along the *b* axis, showing the acetonitrile molecules in the channel. (c) A zigzag arrangement between the layers can be seen along the *a* axis.



Fig. S4 Selected bond distances for the two independent molecules of 1.1.67 hexane, showing distances consistent with distinct catecholate and semiquinonate redox character for the two *o*-dioxolene sites in molecule 1 (top), but intermediate distances in molecule 2 (bottom).



Fig. S5 (a) Structural representation of a ligand…ligand intermolecular π - π stacking interaction (3.42 Å) in **1**·1.67hexane. (b) A crystal packing diagram of **1**·1.5hexane along the *a* axis at 130 K.



Fig. S6 Thermogravimetric analysis plots for the unground (black) and ground (red) forms of 1.0.5py and for desolvated 1 from 1.2MeCN (blue).



Fig. S7 Plot of photo-induced fraction versus time for **1**·0.5py irradiated at 9 K with 532 nm light.

Table S1 Transition temperatures $(T_{1/2})$, enthalpy changes (ΔH) and entropy changes (ΔS)

for thermally-induced VT transitions in Co complexes

Compound ^{<i>a,b</i>}	$T_{1/2} / K$		$\Delta H / \text{kJ mol}^{-1}$		$\Delta S / J \text{ mol}^{-1} \text{K}^{-1}$		
	Solid	Solution	Solid	Solution	Solid	Solution	References
[Co(3,5-DBCat)(3,5-DBSQ)(2,2'-bpy)]	325	275	32	33.9	98	124	4
[Co(3,5-DBCat)(3,5-DBSQ)(2,2'-bpy)]		277.0		36.56		133.1	5
[Co(3,5-DBCat)(3,5-DBSQ)(phen)]		226.6		26.77		118.1	5
[Co(3,5-DBCat)(3,5-DBSQ)(Me ₂ bpy)]		286.6		38.36		133.8	5
[Co(3,5-DBCat)(3,5-DBSQ)(Ph ₂ bpy)]		350		21.33		60.6	5
$[Co(TCCat)(Me_3tpa)]^+$		250		31.2		125	27
1.0.5py	250		20.7		82.7		this work

^{*a*} Low temperature formulation. ^{*b*} 2,2'-bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, Me₂bpy = 4,4'-dimethyl-2,2'-bipyridine, Ph₂bpy = 4,4'-diphenyl-2,2'-bipyridine, TCCatH₂ = tetrachlorocatechol, Me₃tpa = tris(6-methyl-2-pyridylmethyl)amine.

Authors' responses to checkcif ALERT A's.

1. Alert A's relating to theta (max)/wavelength for: Compound_1_pyridine_130K_b.cif Compound_1_pyridine_200K_b.cif Compound_1_pyridine_273K_b.cif Compound_1_pyridine_rt_b.cif Compound_1_hexane_130K.cif Compound_1_hexane_RT.cif

Crystals corresponding to the above cif's were found to be weakly diffracting and as a result, reflections did not extend out as far in theta as what would normally be considered desirable. This led to the following level A alert being generated by the CHECKCIF program:

The value of sine(theta_max)/wavelength is less than 0.550 Calculated sin(theta_max)/wavelength =

The cif's for each of these structures contains a comment relating to the low theta (max) values in the "experimental special details" (_exptl_special_details) section of the cif.

2. Alert A relating to a properly connected set for Compound_1_hexane_130K.cif

The checkcif program operating on the cif, Compound_1_hexane_130K.cif indicates that the coordinates for the crystal do not form a properly connected set. The alert has arisen because of the way the disordered solvent has been modelled.

3. Alert A's relating to molecular weights and solvent accessible voids for Compound_1_hexane_130K.cif

The checkcif program operating on the cif, Compound_1_hexane_rt.cif indicates the following level A alerts (in addition to the alert relating to the sine θ_{max} /wavelength alert:

These three alerts arise from the fact that the highly disordered solvent (at room temperature) could not be satisfactorily modelled. As a result, the SQUEEZE routine within PLATON was employed to remove the contribution of the solvent to the diffraction pattern. A consequence of this is that the checkcif program recognizes voids within the crystals that are in fact occupied by the highly disordered solvent. The absence of solvent from the model results in a discrepancy between the molecular weight based on assigned atoms and the actual molecular weight including the solvent molecules.

A comment relating to the use of the SQUEEZE routine appears in the "refinement special details" section (_refine_special_details) of the cif.