Supporting information to accompany

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

Yanyan Mulyana, a Giordano Poneti, b Boujemaa Moubaraki, c Keith S. Murray, c Brendan F. Abrahams, c Lorenzo Sorace d and Colette Boskovic a

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 1·1.67hexane, 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>
<thead>
<tr>
<th>Compound</th>
<th>$T_{1/2}$ / K</th>
<th>$\Delta H$ / kJ mol$^{-1}$</th>
<th>$\Delta S$ / J mol$^{-1}$ K$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(3,5-DBCat)(3,5-DBSQ)(2,2'-bpy)]</td>
<td>325</td>
<td>275</td>
<td>32</td>
<td>33.9</td>
</tr>
<tr>
<td>[Co(3,5-DBCat)(3,5-DBSQ)(2,2'-bpy)]</td>
<td>277.0</td>
<td>275</td>
<td>32</td>
<td>36.56</td>
</tr>
<tr>
<td>[Co(3,5-DBCat)(3,5-DBSQ)(phen)]</td>
<td>226.6</td>
<td>226.6</td>
<td>26.77</td>
<td>118.1</td>
</tr>
<tr>
<td>[Co(3,5-DBCat)(3,5-DBSQ)(Me2bpy)]</td>
<td>286.6</td>
<td>286.6</td>
<td>38.36</td>
<td>133.8</td>
</tr>
<tr>
<td>[Co(3,5-DBCat)(3,5-DBSQ)(Ph2bpy)]</td>
<td>350</td>
<td>350</td>
<td>21.33</td>
<td>60.6</td>
</tr>
<tr>
<td>[Co(TCCat)(Me3tpa)]</td>
<td>250</td>
<td>250</td>
<td>31.2</td>
<td>125</td>
</tr>
<tr>
<td>1·0.5py</td>
<td>250</td>
<td>250</td>
<td>20.7</td>
<td>82.7</td>
</tr>
</tbody>
</table>

* 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, TCCatH$_2$ = 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_pyrine_130K_b.cif
   Compound_1_pyrine_200K_b.cif
   Compound_1_pyrine_250K_b.cif
   Compound_1_pyrine_273K_b.cif
   Compound_1_pyrine_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:

   ALERT: The ratio of given/expected molecular weight as calculated from the _atom_site* data lies outside
   the range 0.90 <> 1.10
   PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure !
   PLAT043_ALERT_1_A Check Reported Molecular Weight .................. 2404.05

   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.