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Redox coupled-spin crossover in cobalt β-diketonate complexes: Structural, electrochemical and computational studies

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ABSTRACT

Structural, electrochemical, spectroelectrochemical, magnetic and spectroscopic studies are reported for the octahedral cobalt β -diketonate complexes, [Co(β -diketonate)₂(N-N)] { β -diketonate = 2,2,6,6-tetramethylheptane-3,5-dionate (tmhd); N–N = 1,10-phenanthroline (phen) 1, 2,2'-bipyridine (2,2'-bpy) 2 and dimethylaminoethylamine (dmae) **3**; β-diketonate = 1,3-diphenylpropane-1,3-dionate (dbm); N-N = phen 4, 2,2'-bpy 5, dmae 6}. X-ray crystallographic studies of the redox pair $[Co(tmhd)_2(2,2'$ bipy) $|^{0/+} 2/2^+$ show a shortening of the Co-ligand bond lengths by between 0.18 and 0.22 Å upon oxidation and a significantly more regular octahedral geometry around the cobalt in the cation consistent with spin crossover in addition to a change in oxidation state. Cyclic voltammetry of **1-6** reveals an irreversible one-electron oxidation to Co^{III} with large peak separations between the oxidation and reduction peaks, indicative of redox coupled-spin crossover (RCSCO); i.e. $[Co(\beta-diketonate)_2(N-N)]$ (S = 3/2) \leftrightarrow $[Co(\beta-diketonate)_2(N-N)]$ (S = 3/2) $(O(\beta-diketonate)_2(N-N)]$ (S = 3/2) tonate)₂(N-N)]⁺ + e^{-} (S = 0). Moreover, the complexes represent rare examples of RCSCO species with a CoO_4N_2 coordination sphere. The tmhd complexes are more easily oxidized than the respective dbm analogues with the oxidation peak potentials in the order bipy < phen < dmae. Oxidation of 1-6 with AgBF₄ yields the corresponding Co^{III} cations, $[Co(\beta-diketonate)_2(N-N)]BF_4$ 1⁺-6⁺ which has been confirmed by ¹H NMR spectroscopy. Spectroelectrochemistry of the redox pairs $[Co(\beta-diketonate)_2(N-N)]^{0/+}$ is consistent with the isolated compounds being identical to the species formed at the electrode. Theoretical studies reveal that the SOMO is essentially metal *d*-orbital and β -diketonate based, consistent with the strong effect of the β -diketonate ligand on the oxidation potential. In addition, there are substantial changes in the relative stabilities of the various spin states compared with $[Co(tacn)_2]^{2+/3+}$ such that the high spin states become more accessible. The above results are consistent with a square scheme mechanism. © 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Spin crossover is one of the most interesting and widely studied phenomena of transition metal complexes in part due to the possible applications of such complexes in fields such as molecular electronics, memory storage and display devices [1–4]. In principle, a coordination complex with any electron configuration from d^4-d^7 may exhibit spin crossover but the most extensively studied systems are those of d^6 Fe^{II} [5–18]. Moreover, in most reported cases the iron center is surrounded by six nitrogen donors as this provides the intermediate ligand field required for spin crossover (e.g. [Fe(phen)₂(NCS)₂]) [19]. Unlike Fe^{II}, spin crossover in cobalt(II) complexes is rather rare with $[Co(bipy)_3]^{2+}$ and $[Co(terpy)_2]^{2+}$ as perhaps the best known examples [20–23].

While spin crossover systems have been widely studied, comparatively little attention has been given to reactions in which the spin crossover is coupled to electron transfer. This is surprising given that reactions in which electron transfer accompanied by a change in spin state are widespread in both chemistry and biology [2–4,24–27]. For instance in cytochrome P450, substrate binding produces a change in spin state of the Fe^{III} heme active site thereby shifting the redox potential and triggering an electron transfer which initiates the catalytic cycle of the enzyme [28,29]. Further examples include the iron-molybdenum cofactor of nitrogenase and cytochrome *c* peroxidases [30–32]. In relation to coordination chemistry the oxidation of high spin (HS) Co^{III} to low spin (LS) Co^{III} is a well known example of redox coupled-spin crossover (RCSCO) [33]. As with the spin crossover complexes discussed earlier most



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RCSCO complexes studied have N₆ coordination environments. Furthermore, although the mechanism of such reactions has been debated for many years it is still unclear whether the reaction proceeds in a concerted fashion or via higher energy spin state intermediates [34–41]. However, recently Schultz and co-workers have shown that the reduction of $[Co(tacn)_2]^{3+}$ (tacn = 1,4,7-triazacyclononane) may proceed through a high energy spin state intermediate [42–44].

In this paper we report the synthesis of a series of octahedral cobalt β -diketonate complexes, [Co(β -diketonate)₂(N–N)] { β -diketonate = 2,2,6,6-tetramethylheptane-3,5-dionate (tmhd); N-N = 1,10-phenanthroline (phen) 1, 2,2'-bipyridine (2,2'-bpy) 2 and dimethylaminoethylamine (dmae) **3**; β-diketonate = 1,3-diphenylpropane-1,3-dionate (dbm); N-N = phen 4, 2,2'-bpy 5, dmae 6 which are shown to undergo redox coupled-spin crossover. Oxidation of these complexes yields the low spin d⁶ Co^{III} cations [Co(Bdiketonate) $_{2}(N-N)$ ⁺. Structural studies reveal a significant change in Co-ligand bond lengths and a more regular octahedral geometry for the oxidized species. Electrochemical studies support a square scheme mechanism. Moreover, unusually for redox coupled-spin crossover species the complexes possess a CoN₂O₄ coordination sphere rather than the more common CoN₆ coordination environment. Finally, through computational studies we attempt to rationalize the observed behavior in these complexes.

2. Results and discussion

2.1. Synthesis of $[Co(\beta-diketonate)_2(N-N)]$

Reaction of $[Co(tmhd)_2(H_2O)_2]$ or $[Co(dbm)_2(H_2O)_2]$ (tmhd = 2, 2,6,6-tetramethylheptane-3,5-dionate, dbm = 1,3-diphenylpropane-1,3-dionate) and N-N donor ligands in THF or CH₂Cl₂ yields the Co^{II} complexes $[Co(\beta-diketonate)_2(N-N)]$ { β -diketonate = tmhd; N-N = 1,10-phenanthroline (phen) 1, 2,2'-bipyridine (2,2'-bpy) 2 and dimethylaminoethylamine (dmae) **3**; β -diketonate = dbm; N-N = phen 4, 2,2'-bpy 5, dmae 6; Scheme 1}. The complexes are red or orange and air stable. IR spectroscopy of 1-6 shows the v_{CO} band between 1583 and 1596 cm^{-1} indicating that the $\beta\text{-diketonate}$ ligands adopt a chelating coordination mode (Table 1) [45]. Similar bands have been observed in the related Ni analogues which are observed between 1582 and 1595 cm⁻¹ [46]. The two dmae complexes, **3** and **6**, also exhibit $v_{\rm NH}$ bands at 3365 and 3362 cm⁻¹, respectively, and are again almost identical with those of their Ni counterparts. Magnetic susceptibility measurements indicate that the complexes are paramagnetic with μ_{eff} between 4.41 and 5.03 BM consistent with high spin Co^{II} [47].

UV–Vis spectroscopy of the compounds in CH₂Cl₂ supports an octahedral Co^{II} coordination environment with a low intensity band at *ca*. 570 nm which by comparison with [Co(hfac)₂(tmeda)] (hfac = hexafluoroacetylacetonate) is assigned to an overlap between the ⁴T_{1g} (F) \rightarrow ⁴T_{2g} (P) and ⁴T_{1g} (F) \rightarrow ⁴A_{2g} (F) transitions [48]. Additional, very intense bands are found in the UV region which are ascribed to ligand centered $\pi \rightarrow \pi^*$ transitions [49]. Sim-



Scheme 1. Synthesis of [Co(β-diketonate)₂(N-N)].

ilar bands are observed for other $[Co(\beta-diketonate)_2(N-N)]$ (β -diketonate = acac, hfac; N-N = en, 2,2'-bipy, phen) complexes [50,51].

2.2. Synthesis of $[Co(\beta-diketonate)_2(N-N)]^+$

The peak potentials from the electrochemical studies suggested that oxidation of the neutral complexes could be achieved with Ag⁺ (*vide infra*, Table 2). Thus, addition of one equivalent of AgBF₄ to the isolated Co^{II} species affords the cationic complexes $[Co(tmhd)_2(N-N)][BF_4]$ (N–N = phen 1⁺, 2,2'-bpy 2⁺ and dmae 3⁺) and $[Co(dbm)_2(N-N)][BF_4]$ (N–N = phen 4⁺, 2,2'-bpy 5⁺ and dmae 6⁺) as green-brown or purple compounds (Table 1). They may also be prepared in a stepwise, one pot reaction from $[Co(\beta-diketo-nate)_2(H_2O)_2]$ followed by addition of the appropriate ligand and subsequent addition of AgBF₄ giving 1⁺-6⁺. The v_{CO} of 1⁺-6⁺ shift to lower wavenumbers by *ca.* 40 or 70 cm⁻¹ for the tmhd and dbm complexes respectively. Related $[Co(acac)_2(N-N)]^+$ (N–N = 2,2'-bpy, en) complexes show v_{CO} bands at 1524 and 1528 cm⁻¹ confirming that the Co^{III} complexes have been formed [52–54].

The cationic complexes despite their different colors exhibit very similar electronic spectra to **1–6** with a band at *ca*. 550 nm which by comparison with $[Co(acac)_2(N-N)]^+$ (N–N = en, 2,2'-bipy, phen) is assigned to the ${}^{1}A_{1g}$ (F) $\rightarrow {}^{1}T_{1g}$ transition [52–54]. As with the neutral complexes additional charge transfer transitions are evident below 350 nm. The band at *ca*. 290 nm for **1**⁺, **2**⁺, **4**⁺ and **5**⁺, is assigned to an MLCT transition while the other bands are assigned to β -diketonate $\pi \rightarrow \pi^*$ transitions [52].

2.3. NMR spectroscopy

The ¹H NMR spectra of **1**⁺–**6**⁺ show sharp, readily identifiable peaks consistent with a low spin d^6 electron configuration (Table 3). The ¹H NMR spectra of **1**⁺, **2**⁺, **4**⁺ and **5**⁺ show signals in the aromatic region consistent with the presence of coordinated phen and bipy ligands and are assigned on the basis of coupling constants, integration values and comparison with the related [Co(acac)₂(N–N)]⁺ (N–N = 2,2'-bipy and phen) complexes [52,53]. As expected we observe a single resonance for the central β-diketonate proton indicating that the β-diketonate ligands are magnetically equivalent. In the case of **1**⁺ and **2**⁺ there are two singlets between 1.32 and 0.80 ppm for the *t*-butyl groups. The phenyl protons for the dbm ligands in **4**⁺ and **5**⁺ are observed between 6.97 and 8.04 ppm as a series of multiplets.

The dmae complexes show more complex spectra as a result of the asymmetry of the dmae ligand. This is most clearly evidenced by the presence of two singlets for the β -diketonate hydrogen confirming the magnetic inequivalence of the β -diketonate ligands. Moreover, in the case of **3**⁺ there are three resonances for the *t*-butyl groups integrating in a ratio of 2:1:1 indicating that two of the singlets are coincident. As with **4**⁺ and **5**⁺, the phenyl protons for the dbm ligands of **6**⁺ are split into a number of doublets and multiplets between 7.37 and 8.10 ppm. The dmae ligands show two sharp singlets for the methyl groups but four broad resonances for the individual protons on the ligand's backbone. The amino protons are not observed in both cases possibly due to H-bonding [46].

2.4. Structural studies of a Co^{II/III} redox pair

Crystals of the redox pair $[Co(tmhd)_2(2,2'-bipy)]^{0/+} 2/2^+$ were grown by allowing diffusion of hexane into a concentrated solution of the complex in CH₂Cl₂. The structures are shown in Fig. 1; selected bond lengths and angles are given in Table 4 and crystallographic data in Table 5. The structure of 2⁺ contains two independent molecules in the unit cell, however the bonds lengths and angles in these two molecules are virtually identical differing from each other by less than 0.005 Å or 1° and thus the discussion is limited to only

Table 1

IR and UV–Vis spectroscopic data for $[Co(\beta-diketonate)_2(N-N)]^{0/+}$ complexes.

Complex	Color	$IR (cm^{-1})^a$		$\lambda/\mathrm{nm}(\log \varepsilon/\mathrm{M}^{-1} \mathrm{cm}^{-1})$	
		vc=o	v_{N-H}		
[Co(tmhd) ₂ (phen)] 1	Deep red	1589	-	232 (4.60), 268 (4.62), 290 (4.37 sh)	
[Co(tmhd) ₂ (2,2'-bpy)] 2	Orange	1587	-	284 (4.49)	
$[Co(tmhd)_2(dmae)]$ 3	Deep red	1583	3365	282 (4.18)	
$[Co(dbm)_2(phen)]$ 4	Red	1595	-	232 (4.73), 268 (4.71), 352 (4.52)	
[Co(dbm) ₂ (2,2'-bpy)] 5	Red	1596	-	247 (4.51), 350 (4.49)	
[Co(dbm) ₂ (dmae)] 6	Red	1594	3362	249 (4.35), 349 (4.47)	
$[Co(tmhd)_2(phen)]^+$ 1 ⁺	Dark red	1543	-	234 (4.74), 268 (4.60), 300 (4.29 sh)	
$[Co(tmhd)_2(2,2'-bpy)]^+ 2^+$	Maroon	1545	-	236 (4.73), 298 (4.38), 342 (3.81)	
$[Co(tmhd)_2(dmae)]^+$ 3 ⁺	Pastel purple	1560	3310	238 (4.65), 266 (4.41 sh), 334 (3.81 sh)	
			3264		
$[Co(dbm)_2(phen)]^+$ 4 ⁺	Olive green	1524	-	230 (4.69), 274 (4.88), 296 (4.83 sh), 386 (4.20)	
$[Co(dbm)_2(2,2'-bpy)]^+$ 5 ⁺	Brown green	1524	-	230 (4.70), 292 (4.83), 388 (4.23)	
$[Co(dbm)_2(dmae)]^+$ 6 ⁺	Olive green	1525	3320	230 (4.48), 282 (4.61), 388 (4.11)	
	-		3264		

^a As KBr discs.

Table 2

Cyclic voltammetric data of [Co(β-diketonate)₂(N-N)].

Complex	Peak potential (V) ^a			
	Epa ₁	Epc_1	Epc ₂	
[Co(tmhd) ₂ (phen)] 1	-0.15	-0.27	-1.18	
[Co(tmhd) ₂ (2,2'-bpy)] 2	-0.11	-	-1.08	
[Co(tmhd) ₂ (dmae)] 3	-0.13	-	-1.32	
[Co(dbm) ₂ (phen)] 4	0.03	-0.37	-0.98	
[Co(dbm) ₂ (2,2'-bpy)] 5	-0.07	-0.38	-0.61	
[Co(dbm) ₂ (dmae)] 6	0.06	-0.43	-1.21	
$[Co(tmhd)_2(phen)]^+$ 1 ⁺	-0.17	-0.34	-1.38	
$[Co(tmhd)_2(2,2'-bpy)]^+ 2^+$	-0.24	-0.38	-1.41	
[Co(tmhd) ₂ (dmae)] ⁺ 3 ⁺	-0.08	-0.31	-1.53	
$[Co(dbm)_2(phen)]^+$ 4 ⁺	0.00	-0.22	-0.86	
$[Co(dbm)_2(2,2'-bpy)]^+$ 5 ⁺	-0.06	-	-0.73	
$[Co(dbm)_2(dmae)]^+$ 6 ⁺	-0.17	-	-0.72	

^a All measurements were performed at 298 K, in a dried and degassed CH_2Cl_2 0.1 M [NBuⁿ₄][PF₆] solution; scan rate 100 mV s⁻¹; calibrated with [FeCp₂], and reported relative to the [FeCp₂]^{0/+} couple.

one of these independent molecules. The structures of **2** and **2**⁺ are broadly similar to each other possessing an octahedral CoO₄N₂ coordination environment. The most striking change upon oxidation is a shortening of the metal ligand bond lengths by between 0.18 and 0.22 Å. Similar differences are observed for the $[Co(2,2'-bipy)_3]^{2+/3+}$, $[Co(phen)_3]^{2+/3+}$ and $[Co(en)_3]^{2+/3+}$ redox pairs where the difference is 0.19 Å in all cases [55,56].

Interestingly, the degree of distortion around the metal center is also markedly different with the cation, 2^+ exhibiting a much more regular octahedral environment. The parameter, Σ , is the sum of the deviations from 90° of all the *cis* angles in the coordination sphere

and is often used to quantify octahedral distortion [57]. A related parameter, Θ , is defined as the sum of all the deviations from 60° of the 24 angles between the triangular planes within the octahedron and as well as quantifying octahedral distortion is also found to directly correlate with the temperature at which spin crossover occurs [58]. In this redox pair Σ is 86 and 34 for **2** and **2**⁺, respectively, thus $\Delta \Sigma = 52$ while $\Delta \Theta = 180$ consistent with the spin change that occurs upon oxidation. Iron spin crossover compounds also exhibit significant distortion in the high spin state which is reduced upon spin crossover. However, in the $[Fe(NCS)_2(N-N)_2]$ series $\Delta\Sigma$ = 33 and $\Delta\Theta$ = 79 on average, suggesting that redox coupledspin crossover results in an even greater reduction in octahedral distortion [58]. In addition, while the tmhd ligands bind in an angular fashion to the cobalt center in 2 they exhibit a planar coordination mode in 2^+ as demonstrated by the change in the β angle (see Table 4). This profound difference in bond lengths and geometry around the metal is due to a spin change in addition to an increase in oxidation state which result in complete depopulation of the antibonding e_{g}^{*} orbitals. This combined change in spin and oxidation state is known as redox coupled-spin crossover.

2.5. Electrochemistry

The complexes **1–6** have been studied by cyclic voltammetry (CV) and square wave voltammetry in dry CH_2Cl_2 under anaerobic conditions and reveal irreversible one-electron oxidation. The CV of [Co(tmhd)₂(phen)] **1** is shown in Fig. 2a as a representative example. The cyclic voltammograms (CVs) are broadly similar, exhibiting a single oxidation peak, Epa₁, and in most cases a small reduction peak, Epc₁, followed by a much larger reduction peak,

Table 3 ¹H NMR spectroscopic data of [Co(β-diketonate)₂(N–N)]BF₄ complexes.

Complex	δ (ppm)
[Co(tmhd) ₂ (phen)] ⁺	8.98 (2H, dd, J _{HH} 0.6 Hz, 8.1 Hz, CH ^{Phen}), 8.38 (2H, d, J _{HH} 5.4 Hz, CH ^{Phen}), 8.34 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s, CH ^{Phen}), 8.15 (2H, dd, J _{HH} 8.1 Hz, 5.4 Hz, CH ^{Phen}), 5.91 (2H, s), 5.91
1' [Co(tools d) (2.2)	CHEEREN , 1.31 (18H, S, F-BU), 0.80 (18H, S, F-BU)
$[Co(tmnd)_2(2,2' - 1)]$	8.90 (2H, d, J _{HH} /.8 HZ, H ^{4,} G ³), 8.42 (2H, T, J _{HH} /.8 HZ, 6.3 HZ, H ^{4,} G ³), 8.12 (2H, d, J _{HH} 5.1 HZ, H ^{4,} G ³), 7.70 (2H, T, J _{HH} 6.3 HZ, 5.1 HZ, H ^{4,} G ³), 5.86
bpy)j Z	(2H, S, CH ²¹⁰⁰), 1.32 (18H, S, <i>t</i> -Bu), 0.87 (18H, S, <i>t</i> -Bu)
[Co(tmhd) ₂ (dmae)] ⁺	5.87 (1H, s, CH ^{remual}), 5.80 (1H, s, CH ^{remual}), 4.00 (2H, s, N-CH ₂), 2.80 (2H, s, N-CH ₂), 2.39 (3H, s, N-CH ₃), 1.80 (3H, s, N-CH ₃), 1.21 (18H, s, <i>t</i> -Bu),
3*	1.12 (9H, s, t-Bu), 1.05 (9H, s, t-Bu)
[Co(dbm) ₂ (phen)] ⁺	9.01 (2H, dd, J _{HH} 8.1 Hz, 0.9 Hz, CH ^{Phen}), 8.70 (2H, d, J _{HH} 5.1 Hz, CH ^{Phen}), 8.40 (2H, s, CH ^{Phen}), 8.12 (2H, dd, J _{HH} 8.1 Hz, 5.1 Hz, CH ^{Phen}), 8.04 (4H, m,
4*	H ^{Ph}), 7.60–7.55 (6H, m, H ^{Ph}), 7.50–7.40 (6H, m, H ^{Ph}), 7.32–7.28 (4H, m, H ^{Ph}), 7.01 (2H, s, CH ^{central})
[Co(dbm) ₂ (2,2'-	9.03 (2H, d, J _{HH} 7.50 Hz, H ^{6, bpy}), 8.47 (4H, m, H ^{6, bpy} , H ^{3, bpy}), 7.98 (4H, d, J _{HH} 7.20 Hz, H ^{Ph}), 7.70 (2H, t, J _{HH} 6.90 Hz, H ^{4, bpy}), 7.64 (4H, d, J _{HH}
bpy)]* 5*	7.20 Hz, H ^{ph}), 7.55–7.34 (12H, m, H ^{ph}), 6.97 (2H, s, CH ^{central})
[Co(dbm) ₂ (dmae)] ⁺	8.10 (2H, d, J _{HH} 6.90 Hz, H ^{Ph}), 7.97 (3H, m, H ^{Ph}), 7.91 (2H, d, J _{HH} 7.2 Hz, H ^{Ph}), 7.71 (2H, d, J _{HH} 7.50 Hz, H ^{Ph}), 7.59–7.50 (9H, m, H ^{Ph}), 7.42–7.37 (4H,
6+	m, H ^{Ph}), 6.97 (1H, s, CH ^{central}), 6.81 (1H, s, CH ^{central}), 4.70 (1H, broad, s, N-CH ₂), 4.50 (1H, broad, s, N-CH ₂), 3.20 (1H, broad, s, N-CH ₂), 2.80 (1H,
	broad, s, N-CH ₂), 2.56 (3H, s, N-CH ₃), 2.01 (3H, s, N-CH ₃)



Fig. 1. POV-Ray thermal ellipsoid plot of 2 (left) and 2* (right) with ellipsoids at 50%. Only selected atoms are labeled and hydrogen atoms are omitted for clarity.

Table 5

 Table 4

 Selected bond lengths (Å) and angles (°) of $[Co(tmhd)_2(2,2'-bipy)]^{0/+} 2/2^+$.

	2 ^a	2*	Δ Co-L	$\Delta \angle$
Co-01	2.048(1)	1.867(5)	0.181	
Co-02	2.051(1)	1.871(5)	0.180	
Co-O3	-	1.862(4)	0.186	
Co-04	-	1.865(5)	0.186	
Co-N1	2.128(1)	1.915(5)	0.213	
Co-N2	-	1.911(5)	0.218	
N(1)-Co-N(2) {N(1)*}	76.02(5)	83.7(2)		7.68
N(1)-Co-O(1) {O(2)}	80.91(4)	86.6(2)		5.69
N(1)-Co-O(2) {O(1)}	161.69(5)	177.0(2)		15.31
N(1)-Co-O(3) {O(2)*}	102.44(4)	93.5(2)		8.94
$N(1)-Co-O(4) \{O(1)^*\}$	94.87(5)	90.4(2)		4.47
N(2)-Co-O(1)	-	88.7(2)		
N(2)-Co-O(2)	-	93.7(2)		
N(2)-Co-O(3)	-	176.5(2)		
N(2)-Co-O(4)	-	87.4(2)		
O(1)-Co-O(2)	85.73(4)	94.8(2)		9.07
O(1)-Co-O(3) {O(2)*}	97.96(4)	89.2(2)		8.76
O(1) {O(2)}-Co-O(4) {O(2)*}	175.82(4)	175.3(2)		0.52
O(1)-Co-O(3) {O(1)*}	91.52(4)	89.2(2)		2.22
O(2)-Co-O(4)	-	88.1(2)		
O(3)-Co-O(4)	-	94.7(2)		
β	23.5	10.3		13.2
	23.5	13.4		10.1
Σ	86	34		52
Θ	223	43		180

^a The labels for symmetry related atoms in **2** are given in parenthesis.

Epc₂, which is widely separated from Epa₁ (Table 2). The irreversibility of the redox processes, contrasts with the Ni analogues which show either quasi-reversible oxidation or completely chemically irreversible oxidations with no corresponding reduction peaks [46], suggests that the oxidation/reduction is accompanied by a structural and electronic rearrangement. The electrochemical data may suggest that the oxidation of 1-6 to Co^{III} (Epa₁) initially produces a high spin Co^{III} intermediate (Epc₁) which can be re-reduced close to the oxidation peak, Epa₁. Epc₁ is presumably the cathodic partner to the anodic peak represented by Epa1. The high spin Co^{III} species rapidly undergoes spin crossover to the more stable low spin Co^{III} isomer which is reduced at a significantly more negative potential (Epc₂) resulting in a wide separation between the oxidation and reduction peak potentials, Epa₁ and Epc₂. The absence of a corresponding peak for the low spin Co^{II} intermediate (Epa₂) may be due to more rapid spin crossover in this case. It is important to note that a concerted pathway directly from high spin Co^{II} to low spin Co^{III} is also consistent with the above data. The redox behavior of these complexes is in agreement with the structural studies and indicative of redox coupled-spin crossover [59,60]. Redox coupled-spin Crystallographic data and structure refinement for complexes $[\rm Co(tmhd)_2(2,2'-bipy)]^{0/*}~2/2^*.$

	2	2*
Formula	$C_{32}H_{46}CoN_2O_4$	C ₆₄ H ₉₂ B ₂ Co ₂ F ₈ N ₄ O ₈
Molecular weight (g mol ⁻¹)	581.64	1336.90
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$
a (Å)	11.2757(2)	25.8255(14)
b (Å)	30.2006(6)	14.4006(7)
<i>c</i> (Å)	9.9551(2)	20.2612(10)
α (°)	90	90
β(°)	111.3550(10)	91.059(3)
γ(°)	90	90
T (K)	100(2)	100(2)
Cell volume (Å ³)	3157.29(11)	7533.9(7)
Ζ	4	4
Absorption coefficient (mm ⁻¹)	0.580	0.508
Reflections collected	17040	75018
Independent reflections (R_{int})	3662, 0.015	9163, 0.085
Maximum and minimum transmission	0.746, 0.671	0.746, 0.637
Restraints/parameters	0/223	174/917
Final <i>R</i> indices $[I > 2\sigma(I)]$: R_1 , wR_2	0.032, 0.080	0.081, 0.205

crossover is best described by the square scheme shown in Scheme 2.

The two processes 1 and 3 represent the oxidation and reduction reactions of the individual spin state isomers while processes 2 and 4 represent the spin exchange reactions in the individual oxidation states. Redox coupled-spin crossover has also been observed and extensively studied by Schultz et al. in a series of $[M(tacn)_2]^{2+/3+}$ (M = Fe, Co; tacn = 1,4,7-triazacyclononane) complexes although in this system the redox processes are fully reversible [42-44]. Similar redox behavior to 1-6 has recently been reported in the dimeric complex $[(bpbp)Co_2(O_2P(OPh)_2)_2]^+$ $(bpbp^- = 2,6-bis(N,N'-bis-(2-D_2P(OPh)_2)_2)^+$ picolyl)amino)methyl)-4-tertbutylphenolato) which also shows wide separation of the oxidation and reduction peaks [61]. A similar result is also found in the case of $[(Tp^R)_2Co]^{0/+}$ (Tp^R = Tp, pzTp and Tp*) where increasing steric bulk results in a corresponding increase in irreversibility [62]. Comparisons between [Co(tacn)₂]²⁺ and complexes **1–6** show that the former is oxidized *ca*. 0.9 V more easily than the latter consistent with the greater stability of the Co^{II} oxidation state for the $[Co(\beta-diketonate)_2(N-N)]$ complexes. In contrast, the $[(bpbp)Co_2(O_2P(OPh)_2)_2]^+$ dimer oxidizes at a higher potential, 0.42 V (vs. [FeCp₂]^{0/+}).

The oxidation peak potentials for **1–6** are *ca*. 0.54 V more negative than the related Ni compounds [46]. A similar difference in the redox potentials has also been observed in the two series $[M(tacn)_2]^{2+/3+}$ and $[(Tp^R)_2M]^{0/+}$ ($Tp^R = Tp$, pzTp and Tp^* ; M = Co, Ni) [42,62–64]. Within the two series of **1–6** we find that the tmhd



Fig. 2. Cyclic voltammograms of (a) [Co(tmhd)₂(phen)] 1 (b) [Co(tmhd)₂(phen)]BF₄ 1⁺[BF₄].



Scheme 2. Square scheme of the redox coupled-spin crossover process showing individual spin crossover and electron transfer processes.

complexes are easier to oxidize than the corresponding dbm complexes by *ca*. 0.14 V indicating that the inductive effects of the *t*butyl groups increase the electron density on the metal thereby making it easier to oxidize. A similar trend is observed for the Ni analogues although the difference is larger by *ca*. 0.30 V [46]. The Co complexes show oxidation peak potentials in the order bipy < phen < dmae. This order is surprising given that for the [Ni(β diketonate)₂(N–N)] complexes the dmae compounds are the most easily oxidized which is more in line with the typical electron donating properties of diamine and diimine ligands. The difference in the order of the peak potentials may be the result of the spin change which occurs upon oxidation. The difference in the oxidation and reduction peak potentials ($\Delta E = \text{Epa}_1 - \text{Epc}_2$) varies from 0.54 to 1.06 V with **1–3** exhibiting larger ΔE values than **4–6**, thereby indicating that the greater steric bulk of the *t*-butyl groups results in a reduction in the rate of electron-transfer. Similar observations in the [(Tp^R)₂Co]^{0/+} series are also attributed to steric effects [62]. In the case of [(bpbp)Co₂(O₂P(OPh)₂)₂]⁺ $\Delta E = 1.04$ and 0.61 V for the two redox reactions which agrees well with our findings for **1–6** [61].

It is interesting to note that while the $[Co(tacn)_2]^{2+/3+}$ and $[(Tp^R)_2Co]^{0/+}$ redox pairs have a CoN_6 coordination sphere **1–6** and $[(bpbp)Co_2(O_2P(OPh)_2)_2]^+$ possess CoN_2O_4 and CoN_3O_3 coordination spheres, respectively. The presence of the weaker field oxygen donors would be expected to favor the high spin isomers and may be responsible for the irreversibility seen in these systems. It may also explain why we are able to observe a reduction peak for the high spin Co^{III} intermediate in some of the complexes.

In an attempt to better understand the redox coupled-spin crossover process in complexes 1-6 we undertook cyclic voltammetric studies at high scan rates using a microelectrode. There

was little change in the reversibility of the complexes even at moderately fast scan rates (10 V s^{-1}) consistent with a rapid spin exchange equilibrium and slow electron transfer as is frequently observed in these systems (Fig. 3) [33,60]. This result seems reasonable since going from the high spin to the low spin state does not require any bonds to be broken but rather optimization of the Co-ligand bond lengths. Similar irreversibility at high scans rates is also observed in the [(bpbp)Co₂(O₂P(OPh)₂)₂]⁺ dimer. In addition, studies on a wide range of cobalt am(m)ine systems also reveal slow electron transfer [60].

Despite the fact that redox coupled-spin crossover reactions are well documented the mechanism still remains the subject of considerable debate with a pathway via high energy spin-state intermediates and a concerted pathway both proposed [34–41]. As noted earlier the cyclic voltammograms of **1–6** clearly show the presence of peaks which may be attributable to a high spin Co^{III} intermediate and suggest that the mechanism for the oxidation of **1–6** proceeds via a high spin intermediate. However, it must be stated that at this time we cannot rule out a concerted pathway. Moreover, we cannot definitively prove which high spin intermediate is (*vide infra*) a high spin triplet seems likely. In addition, at all applied scan rates (0.02–10 V s⁻¹) we were unable observe a peak for the potential low spin Co^{III} intermediate further supporting high spin pathway.

The square wave voltammograms show peak potentials similar to those found in the CVs. The slight deviations between the two methods might be due to the dependence of the peak potentials on scan rate noted in the CVs. The peaks also exhibit slight asymmetry consistent with the electrochemical irreversibility observed in the CVs.

The cations 1^+-6^+ were also studied by cyclic voltammetry and show a large reduction peak coupled to a smaller redox couple at a higher potential (Fig. 2b). The peak potentials observed in the cyclic voltammograms are almost identical to those found in the neutral analogues although there are slight deviations. Similar results are noted in the complex [(bpbp)Co₂(O₂P(OPh)₂)₂]³⁺ where shifts of up to 0.18 V are observed [61]. As with **1–6** the peaks for the high spin Co^{III} intermediate are clearly discernable but no peak is apparent (i.e. "Epa₂") for the low spin Co^{II} intermediate. Such behavior is typical of square scheme systems which involve first order isomerization of an initial electrode product to the final observed form [61]. Furthermore, the apparent reversibility of the CVs do not change with concentration a result which rules out significant contribution of the second-order homogeneous cross reaction (i.e. LS Co^{III} + HS Co^{III} \rightarrow LS Co^{III} + HS Co^{III}) to the observed current [65]. In such a reaction, the HS Co^{III} produced by equilibrium 2 in Scheme 2 would react with electrogenerated LS Co^{II}. Thus, the reduction of the LS Co^{III} to HS Co^{II} proceeds by the expected LS Co^{II} intermediate. Similar reasoning leads to the conclusion that the oxidation of the HS Co^{III} to LS Co^{III} proceeds by the observed HS Co^{III} intermediate.

To confirm that the products isolated from the chemical oxidation of **1–6** were the same as those observed in the cyclic voltammograms we undertook IR spectroelectrochemical studies. The results are detailed in Table 6 with a representative difference spectrum shown in Fig. 4. The oxidation of 1-6 are all accompanied by the loss (i.e. downward-pointing features) of the β -diketonate $v_{\rm CO}$ bands at *ca*. 1590, 1570, 1520 and 1500 cm⁻¹ due to the Co^{II} starting materials and a corresponding increase in bands at between *ca*. 1550 and 1520 cm^{-1} due to the Co^{III} products. Bands at frequencies lower than 1500 cm^{-1} are lost due to interference from the electrolyte. Subsequent reduction restores the original spectrum showing (as expected) that the chemical oxidation or reduction is reversible. The shift in the bands to lower wavenumbers mirrors exactly what is observed in the isolated complexes and is consistent with the higher Co^{III} oxidation state. Moreover, the positions of the bands are almost identical between the isolated redox pairs and the results from spectroelectrochemistry confirm that the isolated complexes are the species formed at the electrode. Similar studies on the cationic species 1⁺-6⁺ show an exact opposite trend with bands moving to higher wavenumbers as one would expect. Consistent with the CV results, no features due to HS Co^{III} were observed, consistent with the presence of a very small equilibrium concentration.

2.6. Computational studies

In order to better understand the electronic structure of **1–6**, and their respective cations, and in particular the role of the electronic structure on the redox coupled-spin crossover process we have undertaken DFT calculations [66]. For a given complex, all possible spin states were considered.

The fact that we have structurally characterized $[Co(tmhd)_2 (2,2'-bipy)]$ **2** allows a comparison between the computational and experimental geometries (see Table 7). The computed bond lengths match well with the experimental bond lengths with differences no more than 0.05 Å. The bonds angles show similar agreement between experiment and theory. Good agreements between the X-ray structure and computed geometry of $[Co(tmhd)_2 (2,2'-bipy)]$ in the quartet spin state indicates that the complex



Fig. 3. Cyclic voltammograms of [Co(tmhd)₂(phen)] at scan rates of 50-1600 mV/s.

Table (5
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IR spectroelectrochemical difference data of $[Co(\beta-diketonate)_2(N-N)]$ complexes (cm^{-1}) .

Complex	Bands of species produced	Bands of starting material consumed
$[Co(tmhd)_2(phen)]$ 1 ^a	1552, 1543, 1523	1587, 1572, 1533, 1516, 1505
$[Co(tmhd)_2(2,2'-bpy)]$ 2 ^a	1545, 1527	1588, 1581, 1570, 1518, 1504
[Co(tmhd) ₂ (dmae)] 3 ^a	1557, 1547, 1533	1592, 1582, 1570
[Co(dbm) ₂ (phen)] 4 ^a	1587, 1528	1596, 1564, 1554, 1514
$[Co(dbm)_2(2,2'-bpy)]$ 5 ^a	1530	1597, 1563, 1549
$[Co(dbm)_2(dmae)]$ 6 ^a	1526	1563, 1553
$[Co(tmhd)_2(phen)]^+$ 1 ^{+b}	1589, 1573, 1506	1558, 1548, 1525
$[Co(tmhd)_2(2,2'-bpy)]^+ 2^{+b}$	1587, 1572, 1506	1552 (sh), 1544, 1531, 1496
[Co(tmhd) ₂ (dmae)] ⁺ 3 ^{+b}	1596, 1581, 1569	1546, 1534
$[Co(dbm)_2(phen)]^+$ 4 ^{+b}	1596, 1557, 1552, 1512	1538 (sh), 1529
$[Co(dbm)_2(2,2'-bpy)]^+$ 5 ^{+b}	1597, 1579, 1554, 1513	1530, 1588
[Co(dbm) ₂ (dmae)] ⁺ 6 ^{+b}	1596, 1557, 1516	1588, 1540, 1528

^a Oxidized at *ca*. Epa₁.

^b Reduced at Epc₂.



Fig. 4. IR spectroelectrochemical difference spectra of $[Co(dbm)_2 \ (phen)]BF_4$ $4^{\star}[BF_4].$

exists in a high spin state. It also confirms that the B3LYP/SDD model can be used to describe these types of complexes.

Despite this agreement between the computed and observed bond lengths and angles the stability of the high spin states are known to be routinely overestimated by B3LYP. This is largely due to the fact that B3LYP significantly overestimates the exchange energy [67,68]. One approach to correct this is to reduce the amount of exchange energy in the hybrid functional. Two particularly effective functionals which have been used primarily with spin crossover compounds are B3LYP* and TPSSh where the degree of exchange is 15% and 10%, respectively [68,69]. The results for all three functionals are reported in Table 8.

All calculations confirm the observation that the HS state is the most stable state for the Co^{II} complexes and the LS state is the most stable state for the Co^{III} complexes and as such are consistent with the magnetic susceptibility measurements. In contrast, with the previously studied $[Co(tacn)_2]^{2+/3+}$ redox pair the gas-phase energy difference between the HS and LS states, E(HS)-E(LS), for the neutral Co^{II} complexes is between -8.7 and -17.3 kcal/mol (see Table 7) compared with -0.09 kcal/mol for $[Co(tacn)_2]^{2+}$. In the case of the Co^{III} cations the gap is significantly decreased to between 15.0 and 21.4 kcal/mol (*cf.* 45.3 kcal/mol for $[Co(tacn)_2]^{3+}$). As expected reducing the amount of exchange energy results in a re-ordering of the quintet and triplet state of the Co^{III} cations in the case of the B3LYP* and TPSSh functionals compared to the B3LYP functional, although the difference between the quintet and triplet state is still very small. It follows that as the errors often

Table 7

Selected computed and X-ray crystallographically determined bond lengths (Å) and bond angles (°) for [Co(tmhd)₂(2,2'-bipy)] **2**. See Fig. 1 for the numbering scheme.

2	X-ray	Doublet	Diff. ^a	Quartet	Diff. ^a
Co-01	2.048	2.144	0.10	2.0589	0.01
Co-02	2.051	1.948	0.10	2.0680	0.02
Co-N1	2.128	1.946	0.18	2.1339	0.01
C1-01	1.269	1.308	0.04	1.3027	0.03
C7-02	1.261	1.293	0.03	1.3002	0.04
C1-C6	1.403	1.412	0.01	1.4159	0.01
C6-C7	1.407	1.425	0.02	1.4201	0.01
01-Co-02	85.73	88.40	2.67	85.57	0.16
02-Co-02*	175.82	176.99	1.17	176.84	1.02
01-Co-02*	91.52	89.43	2.09	92.53	1.01
01-Co-N1	94.87	93.53	1.32	95.85	0.98
01-Co-N1*	161.69	175.40	13.79	166.39	4.70
02-Co-N1	102.44	89.37	13.07	93.31	9.31
01-Co-01*	97.96	90.44	7.52	97.62	0.34
N1-Co-N1*	76.02	82.53	6.51	76.45	0.43

^a Difference between the X-ray crystallographic and optimized structure.

associated with spin crossover calculations are ca. 3 kcal/mol, even for the state-of-the-art TPSSh functional [67], we can only conclude that the triplet and quintet states lie close to each other in energy. The differences between E(HS)-E(LS) of 1^+-6^+ and $[Co(tacn)_2]^{3+}$ are simply explained by the presence of the lower field β-diketonate ligands which are better able to stabilize the HS states. The thmd ligand stabilizes the HS state compared to the LS state to a greater extent than the dbm ligand. Interestingly, the phen ligand stabilizes the HS state most in comparison with the other N-N ligands. This might be due to a $d-\pi^*$ orbital interaction from a low-lying π^* orbital of the phen ligand. The smaller difference between the LS and HS states in 1^+-6^+ compared with $[Co(tacn)_2]^{3+}$ might also explain why we are able to observe the reduction peak for the HS Co^{III} species in some of the electrochemical studies. These studies further suggest that the mechanism for the redox coupled-spin crossover in this system may involve a HS Co^{III} intermediate.

In comparing the different functionals, the TPSSh functional actually yields the largest E(HS)–E(LS) gap for the Co^{II} complexes despite it having the lowest exchange energy contribution (10% exact exchange), while the B3LYP* functional gives a much smaller gap. Friesner and Hughes have recently compared B3LYP and B3LYP* and concluded that while the B3LYP* functional makes the relative energies of all the spin states more positive it doesn't affect the spin states equally and this can lead to B3LYP* actually performing less well than B3LYP [70].

Thus, in this system with a high spin ground state the quartet state undergoes a larger change in energy than the doublet state

Table 8

The high-spin and low-spin complex energy difference, E(HS)-E(LS), at B3LYP/SDD, B3LYP*/SDD and TPSSh/SDD level for $[Co(\beta-diketonate)_2(N-N)]$ complexes. For **1⁺-6⁺**, the quintet and triplet (in parenthesis) HS states were considered (kcal mol⁻¹).

Complex	E(HS)-E(LS) ^a	E(HS)-E(LS) ^b	$E(HS)-E(LS)^{c}$
[Co(tmhd) ₂ (phen)] 1	-15.63	-12.40	-17.34
[Co(tmhd) ₂ (2,2'-bpy)] 2	-14.55	-10.32	-15.16
[Co(tmhd) ₂ (dmae)] 3	-12.67	-10.44	-16.84
[Co(dbm) ₂ (phen)] 4	-13.84	-9.79	-14.60
[Co(dbm) ₂ (2,2'-bpy)] 5	-12.80	-8.66	-13.50
[Co(dbm) ₂ (dmae)] 6	-13.26	-10.11	-15.45
[Co(tmhd) ₂ (phen)] ⁺ 1 ⁺	16.12 (16.38)	19.59 (17.84)	15.01 (13.74)
[Co(tmhd) ₂ (2,2'-bpy)] ⁺ 2 ⁺	17.15 (17.19)	20.66 (18.67)	16.10 (14.61)
[Co(tmhd) ₂ (dmae)] ⁺ 3 ⁺	17.41 (17.60)	20.71 (19.05)	16.23 (14.60)
$[Co(dbm)_2(phen)]^+$ 4 ⁺	16.93 (17.31)	20.32 (18.69)	15.82 (14.85)
[Co(dbm) ₂ (2,2'-bpy)] ⁺ 5 ⁺	18.01 (18.16)	21.44 (19.53)	16.92 (15.84)
$[Co(dbm)_2(dmae)]^+$ 6 ⁺	17.93 (16.61)	21.17 (17.92)	16.70 (14.68)

^a B3LYP/SDD.

^b B3LYP*/SDD.

^c TPSSh/SDD.

resulting in a greatly reduced E(HS)-E(LS) gap. For instance, in $[Co(tmhd)_2(phen)]$ **1** the relative energy of the doublet is 730 kcal/mol higher than that of the B3LYP functional while that of the quartet is 733 kcal/mol higher yielding a difference of 3 kcal/mol. However, for the TPSSh functional the difference is only 1 kcal/mol resulting in a E(HS)-E(LS) gap comparable to that predicted by B3LYP. Similar results are found for **2–6**. The tendency of the B3LYP* functional to affect the differences in the changes of the relative energies of the triplet and quintet states



Fig. 5. The SOMO orbital of complexes 1-6.



Fig. 6. The LUMO orbital of complexes 1-6.

typically 4–5 kcal/mol compared to 1–2 kcal/mol for the TPSSh functional. This results in the B3LYP* functional predicting the largest E(HS)-E(LS) gap while the TPSSh functional gives the smallest gap with B3LYP in between. Overall, our results indicate that the state-of-the-art TPSSh functional performs best among the three functionals. The rather poor performance of the B3LYP* functional especially for the Co^{II} complexes is probably due to the fact that unlike most systems where B3LYP* performs well, **1–6** do not exhibit thermal spin crossover and contain principally oxygen donor ligands rather than aromatic nitrogen ligands.

The molecular orbital analysis reveals that in the case of 1-3 and 6 the SOMO is composed of an antibonding interaction between the β -diketonate oxygen *p*-orbitals and the cobalt d_{z2} orbital (see Fig. 5). The dmae complexes also exhibit an additional antibonding interaction between the metal orbital and a hybrid σ donor orbital on the NMe2 nitrogen of the dmae ligand. The SOMO of the related bipy and phen complexes, 4 and 5 are different from the others with a metal d_{xz} orbital involved in a weaker antibonding interaction with the β -diketonate ligands. The significant electron density on the β -diketonate ligands in **1–6** is consistent with the strong influence of the β -diketonate upon the oxidation potentials of the above complexes. In the case of **1**, **2**, **4** and **5** the LUMO is essentially a low lying phen or bipy π^* orbital while for **3** and **6** the absence of such π^* orbitals results in a LUMO which is dominated by a β -diketonate π^* orbital (Fig. 6). Consequently, a much larger SOMO-LUMO gap is observed in the case of the dmae complexes compared with 1, 2, 4 and 5.

3. Conclusions

In summary, six redox-active Co β -diketonate complexes have been prepared in two oxidation states which undergo a redox coupled-spin crossover from high spin d^7 to low spin d^6 which has been confirmed by cyclic voltammetry and spectroelectrochemical studies. Chemical oxidation of the Co β -diketonate compounds permits isolation of the Co^{III} cations which are low spin as shown by NMR spectroscopy. Structural studies of the redox pair show that the cobalt-ligand bond lengths are substantially shorter and the geometry around the cobalt center much less distorted upon oxidation. Electrochemical and computational studies on the redox pairs strongly suggest that the redox coupled-spin crossover in the above complexes proceeds via a square scheme mechanism which does not involve a significant amount of homogenous cross-reaction.

4. Experimental

4.1. Materials

All reactions were conducted in air using HPLC grade solvents. $[Co(tmhd)_2(H_2O)_2]$, and $[Co(dbm)_2(H_2O)_2]$ were prepared by literature methods [71,72]. $[Co(dbm)_2(phen)]$ **4** has previously been made although our synthesis differs from that reported [73]. All other chemicals were purchased from Fluka Chemical Company and used as received. Elemental analyses and ESI–MS were carried out by the staff of the School of Chemistry, University of Bristol, UK. Elemental analyses were carried out on a Eurovector EA3000 analyser. ESI–MS were carried out on a Bruker Daltonics 7.0T Apex 4 FTICR Mass Spectrometer. Magnetic susceptibilities were determined using the Evan's method at 297 K [74].

4.2. Spectroscopy

Infrared spectra, as KBr discs, were recorded on a Perkin-Elmer Spectrum One infrared spectrophotometer in the range 400– 4000 cm⁻¹. Electronic spectra were recorded in CH₂Cl₂ on a Unicam UV300 UV–Vis spectrometer. ¹H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer at 298 K in CDCl₃ with SiMe₄ added as an internal standard.

4.3. X-ray crystallography

Crystal data and data processing parameters for the structures of 2 and 2⁺ are given in Tables 4 and 5. X-ray quality crystals of 2 and 2⁺ were grown by allowing hexane to diffuse into a concentrated solution of the complex in CH₂Cl₂. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 100 K in a stream of cold nitrogen. All diffraction data were collected on a Bruker APEX II area detector with graphite monochromated Mo K α (λ = 0.71073 Å). After data collection, in each case an empirical absorption correction (sadabs) was applied [75], and the structures were then solved by direct methods and refined on all F^2 data using the SHELX suite of programs [76]. In all cases nonhydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters which were ca. $1.2 \times (\text{aromatic CH}) \text{ or } 1.5 \times (\text{Me})$ the equivalent isotropic thermal parameters of their parent carbon atoms. In both structures there was disorder in some of the t-butyl groups and this was modeled by splitting the carbon atoms into two parts. X-SEED was used as a graphical interface with SHELX and pictures were generated using POV-Ray [77,78].

4.4. Electrochemistry

Electrochemical studies were carried out using a palmsensPC Vs 2.11 potentiostat in conjunction with a three electrode cell. The

auxiliary electrode was a platinum rod and the working electrode was a platinum disc (2.0 mm diameter). The reference electrode was a Ag–AgCl electrode. Solutions were 5×10^{-4} M in the test compound and 0.1 M in [NBuⁿ₄][PF₆] as the supporting electrolyte. Under these conditions, $E^{\circ\prime}$ for the one-electron oxidation of [Fe(η -C₅H₅)₂] added to the test solutions as an internal calibrant is 0.52 V. For the electrochemical studies at high scan rates a 50 µm platinum disc microelectrode was used as the working electrode with a silver and platinum wire used as the reference and auxiliary electrode, respectively. Fiber-optic difference IR spectroelectrochemical measurements were obtained as previously described [79]. The cyclic voltammograms of [Co(tmhd)₂(H₂O)₂] and [Co(dbm)₂(H₂O)₂] are presented in Figures S1 and S2 in the supporting information.'

4.5. Calculations

All calculations were performed by using the Gaussian 03 package [66]. The B3LYP, B3LYP* and TPSSh hybrid functional with the Stuttgart/Dresden SDD effective core potential basis set was used in all calculations [80–83]. The geometries of complexes for a given spin state were optimized and verified by performing Hessian calculations. The molecular orbital analyses were then conducted at those geometries [66]. The SOMO and LUMO three-dimensional isosurface plots were generated using the Avogadro program [84]. The atomic coordinates for all computed structures may be found in the supporting information.

4.5.1. [Co(tmhd)₂(phen)] 1

To a stirred purple solution of $[Co(tmhd)_2]$ (0.0826 g, 0.2 mmol) in CH₂Cl₂ (15 cm³), phen (0.0396 g, 0.2 mmol) was added. The orange solution was stirred for 1 hour at room temperature then filtered through celite. The solution was left to slowly evaporate at room temperature yields deep red needle crystals 0.0772 g (64%). Magnetic moment (μ_{eff}/μ_B , 297 K): 4.51. C₃₄H₄₆N₂O₄Co; *Anal.* Calc. C 67.4, H 7.7, N 4.6; found C 67.5, H 7.4, N 5.6.

4.5.2. [Co(tmhd)₂(2,2'-bpy)] 2

To a stirred purple solution of $[Co(tmhd)_2]$ (0.0638 g, 0.15 mmol) in CH₂Cl₂ (5 cm³), 2,2'-bpy (0.0240 g, 0.15 mmol) was added. The orange solution was stirred for 1 h then filtered through celite. The solution was left to slowly evaporate at room temperature yields orange needle crystals 0.0451 g (53%). Magnetic moment (μ_{eff}/μ_B , 297 K): 4.53. C₃₂H₄₆N₂O₄Co; *Anal.* Calc. C 66.1, H 8.0, N 4.8; found C 66.3, H 7.8, N 5.1.

4.5.3. [Co(tmhd)₂(dmae)] 3

To a stirred purple solution of $[Co(tmhd)_2]$ (0.0637 g, 0.15 mmol) in CH₂Cl₂ (10 cm³), dmae (150 µL, 0.15 mmol) was added. The orange solution was stirred for 1 h at room temperature then filtered through celite. The solution was left to slowly evaporate at room temperature yields deep red needle crystals 0.0313 g (54%). Magnetic moment (μ_{eff}/μ_B , 297 K): 4.53. C₂₆H₅₀N₂O₄Co; *Anal.* Calc. C 60.8, H 9.8, N 5.4; found C 52.6, H 8.9, N 5.9. Electrospray ionization (ESI) mass data: *m/z* 513 [M]⁺.

4.5.4. [Co(dbm)₂(phen)] 4

To a stirred red-orange solution of $[Co(dbm)_2]$ (0.0816 g, 0.15 mmol) in THF (20 cm³) at 70 °C, phen (0.0301 g, 0.15 mmol) was added. The deep red solution was stirred for 1 h at room temperature then filtered through celite. The solution was left to slowly evaporate at room temperature yields deep red needle crystals 0.0914 g (88%). Magnetic moment (μ_{eff}/μ_B , 297 K): 5.03. C₄₂H₃₄N₂O₄Co; *Anal.* Calc. C 73.1, H 5.0, N 4.1; found C 73.4, H 4.6, N 4.3. Electrospray ionization (ESI) mass data: *m/z* 686 [M]⁺, 462 [M – dbm]⁺.

4.5.5. [Co(dbm)₂(2,2'-bpy)] 5

To a stirred red-orange solution of $[Co(dbm)_2]$ (0.0811 g, 0.15 mmol) in THF (20 cm³) at 70 °C, 2,2'-bpy (0.0234 g, 0.15 mmol) was added. The deep red solution was stirred for 1 h at room temperature then the solution was left to slowly evaporate at room temperature yields deep red needle crystals 0.1014 g (100%). Magnetic moment (μ_{eff}/μ_B , 297 K): 4.41. $C_{40}H_{30}N_2O_4Co$; *Anal.* Calc. C 72.6, H 4.6, N 4.2; found C 72.6, H 5.3, N 4.1. Electrospray ionization (ESI) mass data: *m/z* 661 [M]⁺, 438 [M – dbm]⁺.

4.5.6. [Co(dbm)₂(dmae)] 6

To a stirred red-orange solution of $[Co(dbm)_2]$ (0.0811 g, 0.15 mmol) in THF (20 cm³) at 70 °C, dmae (150 µL, 0.15 mmol) was added. The orange solution was stirred for 1 h at room temperature then filtered through celite. The solution was left to slowly evaporate at room temperature yields deep red needle crystals 0.0646 g (73%). Magnetic moment (μ_{eff}/μ_B , 297 K): 4.98. C₃₄H₃₄N₂O₄Co; *Anal.* Calc. C 68.8, H 5.7, N 4.7; found C 68.8, H 5.7, N 5.0. Electrospray ionization (ESI) mass data: *m/z* 593 [M]⁺, 370 [M – dbm]⁺.

4.5.7. [Co(tmhd)₂(phen)][BF₄] 1⁺

To a stirred purple solution of $[Co(tmhd)_2(H_2O)_2]$ (0.2303 g, 0.5 mmol) in CH₂Cl₂ (20 cm³), phen (0.0992 g, 0.5 mmol) was added. The orange solution was stirred for 1 h then AgBF₄ (0.110 g, 0.56 mmol) added. The brown-orange solution was stirred overnight. The dark green solution was filtered through celite then washed with CH₂Cl₂ (3 × 5 cm³). The solvent was removed to dryness. The solid was purified using CH₂Cl₂-diethyl ether to give dark red block crystals yield 0.2120 g (61%). C₃₄H₄₆BCoF₄N₂O₄; *Anal.* Calc. C 59.0, H 6.7, N 4.0; found C 58.7, H 6.9, N 4.3.

4.5.8. $[Co(tmhd)_2(2,2'-bpy)][BF_4] 2^+$

To a stirred purple solution of $[Co(tmhd)_2(H_2O)_2]$ (0.2330 g, 0.5 mmol) in CH₂Cl₂ (20 cm³), 2,2'-bpy (0.0785 g, 0.5 mmol) was added. The orange solution was stirred for 1 h then AgBF₄ (0.110 g, 0.56 mmol) added. The brown-orange solution was stirred overnight. The dark green solution was filtered through celite then washed with CH₂Cl₂ (3 × 5 cm³). The solvent was removed to dryness. The solid was purified using CH₂Cl₂-diethyl ether to give maroon microcrystals yield 0.2138 g (64%). C₃₂H₄₆BCoF₄N₂O₄; *Anal.* Calc. C 57.5, H 6.9, N 4.2; found C 57.5, H 6.9, N 4.6.

4.5.9. [Co(tmhd)₂(dmae)][BF₄] **3**⁺

To a stirred purple solution of $[Co(tmhd)_2(H_2O)_2]$ (0.2298 g, 0.5 mmol) in CH₂Cl₂ (20 cm³), dmae (54.4 µL, 0.5 mmol) was added. The orange solution was stirred for 1 h then AgBF₄ (0.110 g, 0.56 mmol) added. The dark green solution was stirred overnight. The deep purple solution was filtered through celite then washed with CH₂Cl₂ (3 × 5 cm³). The solvent was removed to dryness. The solid was purified using CH₂Cl₂-diethyl ether to give pastel purple microcrystals yield 0.1841 g (61%). C₂₆H₅₀BCoF₄. N₂O₄; Anal. Calc. C 52.0, H 8.4, N 4.7; found C 52.7, H 8.6, N 5.2.

4.5.10. [Co(dbm)₂(phen)][BF₄] 4⁺

To a stirred orange suspension of $[Co(dbm)_2(H_2O)_2]$ (0.1678 g, 0.3 mmol) in CH₂Cl₂ (20 cm³), phen (0.0620 g, 0.3 mmol) was added. The orange solution was stirred for 1 h then AgBF₄ (0.0700 g, 0.36 mmol) added. The olive green solution was stirred overnight. The dark green solution was filtered through celite then washed with CH₂Cl₂ (3 × 5 cm³). The solvent was removed to dryness. The solid was purified using CH₂Cl₂-*n*-hexane to give olive green microcrystals yield 0.1295 g (56%). C₄₂H₃₄BCoF₄N₂O₄; *Anal.* Calc. C 65.0, H 4.4, N 3.6; found C 66.5, H 4.2, N 3.9.

4.5.11. [Co(dbm)₂(2,2'-bpy)][BF₄] 5⁺

To a stirred orange suspension of $[Co(dbm)_2(H_2O)_2]$ (0.1586 g, 0.3 mmol) in CH₂Cl₂ (20 cm³), 2,2'-bpy (0.0470 g, 0.3 mmol) was added. The orange solution was stirred for 1 h then AgBF₄ (0.0646 g, 0.33 mmol) added. The olive green solution was stirred overnight. The dark green solution was filtered through celite then washed with CH₂Cl₂ (3 × 5 cm³). The solvent was removed to dryness. The solid was purified using CH₂Cl₂-*n*-hexane to give green brown microcrystals yield 0.1097 g (51%). C₄₀H₃₀BCoF₄N₂O₄; *Anal.* Calc. C 64.2, H 4.0, N 3.7; found C 65.2, H 4.3, N 3.9.

4.5.12. [Co(dbm)₂(dmae)][BF₄] 6⁺

To a stirred orange suspension of $[Co(dbm)_2(H_2O)_2]$ (0.1718 g, 0.3 mmol) in CH₂Cl₂ (20 cm³), dmae (34.7 µL, 0.3 mmol) was added. The orange solution was stirred for 1 h then AgBF₄ (0.0710 g, 0.36 mmol) added. The olive green solution was stirred overnight. The dark green solution was filtered through celite then washed with CH₂Cl₂ (3 × 5 cm³). The solvent was removed to dryness. The solid was purified using CH₂Cl₂-*n*-hexane to give olive green microcrystals yield 0.1072 g (49%). C₃₄H₃₄BCoF₄N₂O₄; *Anal.* Calc. C 60.0, H 5.0, N 4.1; found C 62.7, H 5.3, N 3.7.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre (CCDC) with CCDC 829130 for **2** and CCDC 829131 for **2**⁺. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.05.037.

References

- [1] J.-F. Létard, P. Guionneau, L. Goux-Capes, Top. Curr. Chem. 235 (2004) 221.
- [2] O. Kahn, C.J. Martinez, Science 279 (1998) 44.
- [3] L. Fabbrizzi, M. Licchelli, P. Pallavicini, Acc. Chem. Rev. 32 (1999) 846.
- [4] M. Venturi, A. Credi, V. Balzani, Coord. Chem. Rev. 185–186 (1999) 233.
- [5] H.A. Goodwin, Coord. Chem. Rev. 18 (1976) 293.
- [6] (a) J.A. Real, A.B. Gaspar, V. Niel, M.C. Muñoz, Coord. Chem. Rev. 236 (2003) 121;
- (b) Y. Garcia, V. Niel, M.C. Muñoz, J.A. Real, Top. Curr. Chem. 233 (2004) 229.
 [7] K.S. Murray, C.J. Kepert, Top. Curr. Chem. 233 (2004) 195.
- [8] A.B. Gaspar, V. Ksenofontov, J.A. Real, P. Gütlich, Chem. Phys. Lett. 373 (2003) 385.
- [9] (a) H. Spiering, T. Kohlhaas, H. Romstedt, A. Hauser, C. Bruns-Yilmaz, P. Gütlich, Coord. Chem. Rev. 190–192 (1999) 629;
 (b) P. Gütlich, A. Hauser, H. Spiering, Angew. Chem., Int. Ed. Engl. 33 (1994) 2024.
- [10] (a) J.A. Real, in: J.P. Sauvage (Ed.), Transition Metals in Supramolecular Chemistry, John Wiley and Sons Ltd., Chichester, 1999, p. 53;
 (b) J.A. Real, A.B. Gaspar, M.C. Muñoz, P. Gütlich, V. Ksenofontov, H. Spiering, Top. Curr. Chem. 233 (2004) 167.
- [11] J.G. Haasnoot, Coord. Chem. Rev. 200 (2000) 131.
- [12] E. Breuning, M. Ruben, J.M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gütlich, E. Wegelius, K. Rissanen, Angew. Chem., Int. Ed. 39 (2000) 2504.
- [13] J.A. Real, E. Andres, M.C. Muñoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, Science 268 (1995) 265.
- [14] G.J. Halder, C.J. Kepert, B. Moubaraki, K.S. Murray, J.D. Cashion, Science 298 (2002) 1762.
- [15] A.M. Greenaway, E. Sinn, J. Am. Chem. Soc. 100 (1978) 8080.

- [16] A.W. Addison, S. Burman, C.G. Wahlgren, O.A. Rajan, T.M. Rowe, E. Sinn, J. Chem. Soc., Dalton Trans. (1987) 2621.
- [17] D. Collison, C.D. Garner, C.M. McGrath, J.F.W. Mosselmans, M.D. Roper, J.M.W. Seddon, E. Sinn, N.A. Young, J. Chem. Soc., Dalton Trans. (1997) 4371.
- [18] E.J. MacLean, C.M. McGrath, C.J. O'Connor, C. Sangregorio, J.W.M. Seddon, E. Sinn, F.E. Sowery, S.J. Teat, G.B.M. Vaughan, N.A. Young, Chem. Eur. J. 9 (2003) 5314.
- [19] K. Madeja, E. König, J. Inorg. Nucl. Chem. 25 (1963) 377.
- [20] R. Sieber, S. Decurtins, H. Stoeckli, C. Evans, D. Wilson, J.A.K. Yufit, S.C. Howard, A. Capelli, A. Hauser, Chem. Eur. J. 6 (2000) 361.
- [21] (a) M. Zerara, A. Hauser, Chem. Phys. Chem. 5 (2004) 395;
 (b) A. Hauser, N. Amstutz, S. Delahaye, S. Schenker, A. Sadki, R. Sieber, M. Zerara, Struct. Bond. 106 (2004) 81.
- [22] (a) R. Hogg, R.G. Wilkins, J. Chem. Soc. (1962) 341;
- (b) J.S. Judge, W.A. Baker, Inorg. Chim. Acta 1 (1967) 68.
- [23] B.N. Figgis, E.S. Kucharski, A.H. White, Aust. J. Chem. 36 (1983) 1537.
- [24] W.R. Scheidt, C.A. Reed, Chem. Rev. 81 (1981) 543.
- [25] I. Bertani, H.B. Gray, S.J. Lippard, J.S. Valentine, Bioinorganic Chemistry, University Science Books, Sausalito, CA, 1994.
- [26] S.J. Lippard, J.M. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Balley, CA, 1995.
- [27] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, New York, 1995.
- [28] S.C. Sligar, Biochemistry 15 (1976) 5399.
- [29] E.J. Mueller, P.J. Lioda, S.C. Sligar, in: P.R. Ortiz de Montellano (Ed.), Cytochrome P450: Structure, second ed., Mechanism and Biochemistry, Plenum Press, New York, 1995 (Chap. 3).
- [30] D.C. Rees, M.K. Chan, J. Kim, Adv. Inorg. Chem. 40 (1993) 89.
- [31] B.K. Burgess, D.J. Lowe, Chem. Rev. 96 (1996) 2983.
- [32] H. Lopes, G.W. Pettigrew, I. Moura, J.J.G. Moura, J. Biol. Inorg. Chem. 3 (1998) 632.
- [33] P. Hendry, A. Ludi, Adv. Inorg. Chem. 35 (1990) 117.
- [34] H.C. Stynes, J.A. Ibers, Inorg. Chem. 10 (1971) 2304.
- [35] E. Buhks, M. Bixon, J. Jortner, G. Navon, Inorg. Chem. 18 (1979) 2014.
- [36] D.A. Geselowitz, H. Taube, Adv. Inorg. Bioinorg. Mech. 1 (1982) 391.
 [37] S. Larsson, K. Ståhl, M.C. Zerner, Inorg. Chem. 25 (1986) 3033.
- [38] D.A. Geselowitz, Inorg. Chim. Acta 154 (1988) 225.
- [39] M.D. Newton, J. Phys. Chem. 95 (1991) 30.
- [40] R.D. Shalders, T.W. Swaddle, Inorg. Chem. 34 (1995) 4815.
- [41] T.W. Swaddle, Can. J. Chem. 74 (1996) 631.
- [42] J.W. Turner, F.A. Schultz, Inorg. Chem. 38 (1999) 358.
- [43] J.W. Turner, F.A. Schultz, J. Phys. Chem. B 2002 (2009) 106.
- [44] R.L. Lord, F.A. Schultz, M.-H. Baik, J. Am. Chem. Soc. 131 (2009) 6189.
- [45] K. Nakamoto, In Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B, sixth ed., Wiley, New York, 2009. pp. 96.
- [46] P. Harding, D.J. Harding, W. Phonsri, S. Saithong, H. Phetmung, Inorg. Chim. Acta 362 (2009) 78.
- [47] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, in: Advanced Inorganic Chemistry, sixth ed., John Wiley & Sons, New York, 1999, p. 817.
- [48] G. Bandoli, D. Barreca, A. Gasparotto, C. Maccato, R. Seraglia, E. Tondello, A. Devi, R.A. Fischer, M. Winter, Inorg. Chem. 48 (2009) 82.
- [49] N. Nagashima, S. Kudoh, M. Nakata, Chem. Phys. Lett. 374 (2003) 59.
- [50] D.S. Sankhla, R.C. Mathur, S.N. Misra, J. Inorg. Nucl. Chem. 42 (1980) 489.
- [51] P. Chassot, F. Emmenegger, Inorg. Chem. 35 (1996) 5931.
- [52] R.D. Archer, B.P. Cotsoradis, Inorg. Chem. 4 (1965) 1584.
- [52] R.J. York, W.D. Bonds Jr., B.P. Cotsoradis, R.A. Archer, Inorg. Chem. 8 (1969) 789.
- [54] F. Izumi, R. Kurosawa, H. Kawamoto, H. Akaiwa, Bull. Chem. Soc. Jpn. 48 (1975) 3188
- [55] B.S. Brunschwig, C. Creutz, D.H. Macartney, T.K. Sham, N. Sutin, Faraday Discuss. Chem. Soc. 74 (1982) 113.

- [56] A. Wheeler, C. Brouty, P. Spinat, P. Herpin, Acta Crystallogr., Sect.B Struct. Crystallogr. Cryst. Chem. 831 (1975) 2069.
- [57] P. Guionneau, M. Marchivie, G. Bravic, J.-F. Létard, D. Chasseau, J. Mater. Chem. 12 (2002) 2546.
- [58] M. Marchivie, P. Guionneau, J.-F. Létard, D. Chasseau, Acta Crystallogr., Sect. B 61 (2005) 25.
- [59] J.W. Turner, F.A. Schultz, Coord. Chem. Rev. 219-221 (2001) 81.
- [60] (a) For examples of other Co complexes exhibiting RCSCO see E. Buhks, M. Dixon, J. Jortner, G. Navon, Inorg. Chem. 18 (1979) 2014;
 (b) J.F. Endicott, G.R. Brubaker, T. Ramasami, K. Kumar, K. Dwarakanath, J. Cassel, D. Johnson, Inorg. Chem. 22 (1983) 3754;
 (c) A. Hammershøi, D.A. Geselowitz, H. Taube, Inorg. Chem. 32 (1984) 979;
 (d) P.V. Bernhardt, L.A. Jones, P.C. Sharpe, Inorg. Chem. 36 (1997) 2420.
- [61] F.B. Johansson, A.D. Bond, U.G. Nielson, B. Moubaraki, K.S. Murray, K.J. Berry, J.A. Larrabee, C.J. McKenzie, Inorg. Chem. 47 (2008) 5079.
- [62] D.C.L. De Alwis, F.A. Schultz, Inorg. Chem. 42 (2003) 3616.
- [63] K. Wieghardt, W. Schmidt, W. Herrmann, H.J. Kueppers, Inorg. Chem. 22 (1983) 2953.
- [64] H.J. Kueppers, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, J. Weiss, Inorg. Chem. 25 (1986) 2400.
- [65] T.C. Richards, W.E. Geiger, J. Am. Chem. Soc. 116 (1994) 2028.
- [66] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision D.01, Gaussian Inc., Wallingford, CT, 2004.
 [67] K.P. Jensen, J. Cirra, J. Phys. Chem. A 113 (2009) 10033.
- [68] M. Reihner, Inorg. Chem. 41 (2002) 6928.
- [69] J.P. Perdew, J. Tao, V.N. Staroverov, G.E. Scuseria, J. Chem. Phys. 120 (2004) 6898.
- [70] T.F. Hughes, R.A. Friesner, J. Chem. Theory Comput. 7 (2011) 19.
- [71] D. Barreca, C. Massignan, S. Daolio, M. Fabrizio, C. Piccirillo, L. Armelao, E. Tondello, J. Chem. Mater. 13 (2001) 588.
- [72] L.A. Barrios, J. Ribas, G. Aromí, J. Ribas-Ariño, P. Gamez, O. Roubeau, S.J. Teat, Inorg. Chem. 46 (2007) 7154.
- [73] E. Meštrović, B. Kaitner, J. Chem. Crystallogr. 36 (2006) 599.
- [74] D.F. Evans, J. Chem. Soc. (1959) 2003.
- [75] Bruker APEX, SAINT and SADABS 2008, Bruker AXS Inc., Madison, Wisconsin, USA.
- [76] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [77] L.J. Barbour, J. Supramol. Chem. 1 (2001) 189.
- [78] J.A. Atwood, L.J. Barbour, Cryst. Growth Des. 3 (2003) 3.
- [79] M.J. Shaw, R.L. Henson, S.E. Houk, J.W. Westhoff, G.B. Richter-Addo, M.W. Jones, J. Electroanal. Chem. 534 (2002) 47.
- [80] A.D. Becke, J. Chem. Phys. 98 (1993) 1372.
- [81] P.J. Stephens, F.J. Devlin, M.J. Frisch, C.F. Chabalowski, J. Phys. Chem. 98 (1994) 11623.
- [82] T.H. Dunning Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), Modern Theoretical Chemistry, vol. 3, Plenum, New York, 1976, p. 1.
- [83] M. Dolg, U. Wedig, H. Stoll, H. Preuss, J. Chem. Phys. 86 (1987) 866.
- [84] http://avogadro.openmolecules.net/ (accessed 12/22/2009).