

Dicobalt Complexes

Unprecedented Inequivalent Metal Coordination Environments in a Mixed-Ligand Dicobalt Complex

Giacomo Cioncoloni,^[a] Stephen Sproules,^[a] Claire Wilson,^[a] and Mark D. Symes^{*[a]}

Abstract: Bimetallic complexes of the transition metals containing mixed diimine and dithiolate ligands are of fundamental interest on account of their intriguing electronic properties. Almost always, such complexes are isolated as species in which both the metal centers are in identical coordination environments – this means that the two metals often have identical redox properties. In contrast, mixed-diimine/dithiolate bimetallic complexes of the first row transition metals where the two

metals are in dissimilar coordination environments are exceedingly rare, and are only known for nickel. Herein, we report the first ever example of a mixed-diimine/dithiolate dicobalt complex where the two cobalt centers are in different coordination environments. The synthesis of this compound is straightforward, and produces a complex in which the two cobalt centers display very different redox properties.

Introduction

Transition metal complexes containing mixed chelating diimine and dithiolate ligand sets have long been recognized to be of interest on account of their varied physical properties, which include luminescence, non-linear optical behavior, intense coloration and multi-electron redox chemistry.^[1–5] Within this class of compounds, multimetallic complexes containing dithiolene ligands show particular promise for the development of new materials with exciting properties.^[6] In such multimetallic complexes containing dithiolene ligands, the metal centers normally all coordinate to the dithiolene ligands in the same manner, regardless of whether other types of ligand are present or not. This then leads to multimetallic complexes where all the metal ions are in the same coordination environment. For bimetallic species, commonly-observed coordination motifs involving dithiolene ligands include $[M_2(\text{dithiolene})_4]$ ($M = \text{Mn},^{[7,8]}$ $\text{Fe},^{[9,10–11]}$ $\text{Co},^{[7,11,12]}$ $\text{Ni},^{[13,14]}$), $[M_2(\text{dithiolene})_5]$ ($M = \text{Mo}, \text{Rh}, \text{Re},^{[15]}$ and $[M_2(\text{Cp})_2(\text{dithiolene})_2]$ ($\text{Cp} = \text{cyclopentadienyl}, M = \text{V}, \text{Cr}, \text{Fe}, \text{Co}, \text{Mo}, \text{Rh},^{[16]}$ In such complexes, the coordination environment around one metal center is almost always the same as that around the other metal center, and this is especially true when the metals in question are drawn from the first row of the d-block. Indeed, extensive searching of the Cambridge Crystallographic Database (and other databases) returned only two examples of bimetallic complexes of first row

transition metals containing dithiolene ligands where the two metal ions were *not* in the same coordination environment. Both of these are di-nickel complexes reported by Bachman in the late 1990s,^[17] whereby aerial oxidation of the monomeric complex $[\text{Ni}(\text{bdt})(\text{bpy})]$ in DMF leads to the generation of mixtures of $[(\text{bpy})_2\text{Ni}(\text{bdtO}_2)\text{Ni}(\text{bdt})]$ and $[(\text{bpy})_2\text{Ni}(\text{bdtO}_4)\text{Ni}(\text{bdt})]$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{bdt}^{2-} = \text{benzene-1,2-dithiolate}$; Figure 1a). Hence one of the nickel centers in these complexes is octahedral, coordinating to both of the bipyridine ligands and forming interactions with the two dithiolene-derived ligands, whilst the second nickel coordinates only to these dithiolene-derived ligands and adopts a square-planar geometry.

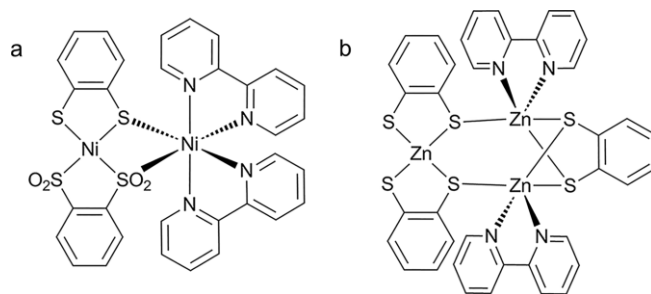


Figure 1. Simplified structures showing the coordination geometry around the metal centers in (a) Bachman's di-nickel complexes and (b) the tri-zinc complexes reported by Wacholtz, Mague and co-workers.

Meanwhile, Wacholtz, Mague, and co-workers have reported two allied tri-zinc complexes where one zinc center is coordinated by two dithiolenes whilst the other two zinc centers each coordinate to one diimine ligand, with a bridging dithiolene ligand and bonds to the dithiolenes on the first zinc as shown in Figure 1b.^[18,19] Beyond these examples, however, we could find no other instances of bimetallic complexes of first row transition metals containing dithiolene ligands where the two metal centers were in different coordination environments (and hence

[a] WestCHEM, School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ, United Kingdom
E-mail: mark.symes@glasgow.ac.uk
<http://www.symeslab.com>

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where the two metal ions could be expected to exhibit differing redox activity).

Herein, we report a dicobalt complex incorporating diimine and dithiolate ligands with an unprecedented coordination motif, whereby the first cobalt center coordinates to one diimine ligand and two dithiolenes, whilst the other cobalt coordinates to two diimine ligands and completes its octahedral geometry by virtue of forming single bonding interactions with both of the dithiolenes that coordinate to the first metal center. The unusual structure of this complex ($[\text{Co}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3]^{2+}$, $[\mathbf{1}]^{2+}$) was determined by single-crystal X-ray diffraction, and NMR and mass spectrometry indicate that this species is also stable in solution. Furthermore, electrochemical analysis of complex $[\mathbf{1}]^{2+}$ indicates that it undergoes a reversible one-electron reduction reaction at very modest cathodic potentials, producing a mixed-valence $\text{Co}^{\text{III}}\text{Co}^{\text{II}}$ species, the likely nature of which we have rationalized using computational methods.

Results and Discussion

Synthesis and Structure of Complex $[\mathbf{1}]^{2+}$

A general route to the synthesis of dicobalt complex $[\mathbf{1}]^{2+}$ is given in Scheme 1. Hence, addition of one equivalent of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to two equivalents of 5,5'-dimethyl-2,2'-bipyridine (Me_2bpy) in methanol resulted in the formation of an orange solution, the color of which rapidly turned to dark green upon the addition of one equivalent of *o*-benzenedithiol under air. After removal of some of the solvent, a dark green solid could be precipitated from the remainder of the dark green solution by addition of diethyl ether. Subsequent recrystallization of this solid from MeOH/diethyl ether then afforded green crystals of $[\mathbf{1}](\text{NO}_3)_2$ suitable for X-ray diffraction (Figure 2).

The connectivity of $[\mathbf{1}]^{2+}$ is evident from Figure 2, which shows that two bipyridine moieties are coordinated in a *cis* fashion around one of the Co centers (Co2), the octahedral geometry of which is completed by coordination to sulfurs from each of the dithiolene ligands. These dithiolene ligands themselves coordinate to the other Co center (Co1) in a *cis* fashion, with the result that one sulfur atom on each dithiolene acts as a bridge between the two cobalt centers. The octahedral coordination environment of Co1 is then completed by bidentate coordination to a unique bipyridine ligand. The Co–S

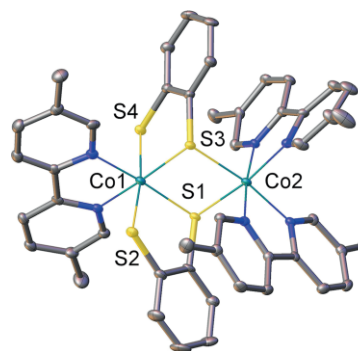
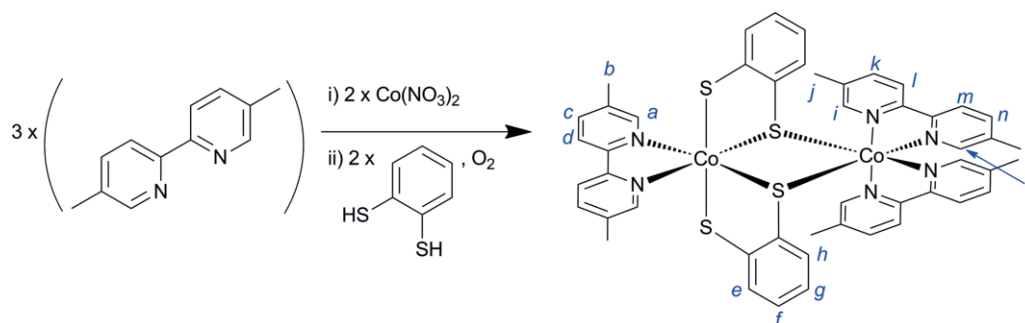


Figure 2. The molecular structure of the di-cationic complex in crystals of $[\text{Co}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3](\text{NO}_3)_2$. Hydrogen atoms, solvent and counterions have been omitted from the structure. Further crystallographic details can be found in the Supporting Information. Color Scheme C = gray, N = blue, S = yellow, Co = cyan. For selected bond lengths and angles, see Table 1.

bond lengths in Figure 2 are $\text{Co1-S1} = 2.2222(7)$ Å, $\text{Co1-S2} = 2.2688(7)$ Å, $\text{Co1-S3} = 2.2251(8)$ Å, $\text{Co1-S4} = 2.2709(8)$ Å, $\text{Co2-S1} = 2.2663(8)$ Å and $\text{Co2-S3} = 2.2620(7)$ Å, and hence the Co–S bond lengths for Co2 are both of approximately the same length as each other (and the same length as between Co1 and the non-bridging sulfurs), whilst the Co–S bond lengths between Co1 and the bridging sulfur atoms are noticeably shorter in length. The coordination sphere for Co2 is nearly identical to that observed in $[\text{Co}(\text{Tab})_2(4,4'\text{-dmbpy})_2](\text{PF}_6)_3$, where Tab is 4-(trimethylammonio)benzenethiolate and 4,4'-dmbpy is 4,4'-dimethylbipyridine.^[20] Most of the angles around Co2 are within the range $85^\circ < \theta < 95^\circ$, with the exception of the S3–Co2–S1, N3–Co2–N4 and N5–Co2–N6 angles, all of which are closer to 82° (see Table 1 and Supporting Information). The maximum deviation from 90° for the bond angles around Co1 are for the N1–Co1–N2 angle (83°) and the N2–Co1–S1 angle (97°). These Co–S–Co angles are therefore similar to related edge-sharing bi-octahedron (ESBO) dicobalt complexes with bridging thiolate ligands.^[21–22,23]

The complex has no Co–Co bond given the long intermetal distance of 3.63 Å. This is a consistent feature of ESBO dicobalt(III) complexes, where the intermetal distance is a function of the donor atoms that comprise the $\{\text{Co}_2\text{X}_2\}$ diamond core, ranging from 2.863(2)–2.951(1) Å for hydroxo-bridged,^[24] 2.885(5)–2.9842(6) Å for alkoxo-bridged,^[25] 2.926(1) Å for imido-bridged,^[26] 2.874(1)–2.977(2) Å for OH/NH₂[–]-bridged,^[27] to



Scheme 1. The general synthetic route followed to synthesize compound $[\mathbf{1}](\text{NO}_3)_2$. Italic letters on the product structure correspond to the ^1H NMR signal assignments in the Experimental Section.

Table 1. Experimental and calculated bond lengths [Å] and angles [°] in $[\text{Co}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3]^z$ ($z = 2+, 1+$).

	$[\text{Co}^{\text{III,III}}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3]^{2+}$ ($S = 0$)		$[\text{Co}^{\text{III,II}}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3]^{1+}$ ($S = 1/2$)	
	exptl.	calcd.	exptl.	calcd.
Co(1)–N(1)	1.940(2)	1.961	1.976	
Co(1)–N(2)	1.952(3)	1.960	1.973	
Co(2)–N(3)	1.961(2)	1.964	1.940	
Co(2)–N(4)	1.983(2)	1.995	2.102	
Co(2)–N(5)	1.986(3)	1.993	1.980	
Co(2)–N(6)	1.957(2)	1.962	1.943	
Co(1)–S(1)	2.2222(7)	2.239	2.247	
Co(1)–S(2)	2.2688(7)	2.289	2.287	
Co(1)–S(3)	2.2251(8)	2.239	2.247	
Co(1)–S(4)	2.2709(8)	2.288	2.280	
Co(2)–S(1)	2.2663(8)	2.302	2.333	
Co(2)–S(3)	2.2620(7)	2.300	2.735	
S(1)–Co(1)–S(2)	89.61(3)	88.4	88.2	
S(3)–Co(1)–S(4)	88.81(3)	88.4	88.6	
S(1)–Co(1)–S(3)	83.83(3)	82.9	86.5	
S(1)–Co(2)–S(3)	82.00(3)	80.2	74.4	
Co(1)–S(1)–Co(2)	97.06(3)	98.4	105.5	
Co(1)–S(3)–Co(2)	97.10(3)	98.5	93.6	
Co(1)⋯Co(2)	3.363	3.438	3.646	
S(1)⋯S(3)	2.971	2.965	3.080	

3.35(1)–3.3441(2) Å with the larger thiolato ligands.^[21–23] Akin to other bimetallic complexes with five chelating ligands,^[15] the chirality about each Co center in $[\mathbf{1}]^{2+}$ is the same ($\Lambda\Lambda$) for each tris-chelate Co ion. The only exception to this rule for bimetallic complexes with five chelating ligands is $[\text{Co}_2(\text{Et}_2\text{dtc})_5]^{1+}$ ($\text{Et}_2\text{dtc}^{1-}$ = diethyldithiocarbamate), where the each Co center has an opposing chirality.^[27a]

The solution-phase ^1H NMR of complex $[\mathbf{1}]^{2+}$ supports the hypothesis that the structure shown in Figure 2 is maintained in solution (see Figures S1 and S2). Hence the bipyridine units around Co2 adopt the characteristic pattern for a *cis* arrangement of these ligands observed in species such as $[\text{Co}^{\text{III}}(\text{bdt})(\text{Me}_2\text{bpy})_2]^{2+}$,^[28] whilst the unique bipyridine coordinated to Co1 sits in a more symmetrical chemical environment. Meanwhile, the peaks corresponding to the dithiolate ligands also show a pattern consistent with their inequivalent binding to the two cobalt centers. Moreover, the fact that the spectrum is sharp and well-resolved serves as good evidence that both the cobalt ions are in the low-spin Co^{III} oxidation state. Meanwhile, mass spectrometry indicates a peak with $m/z = 475.1$, which matches exactly that expected for the $[\text{Co}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3]^{2+}$ ion (ion mass = 950.1174 with a +2 charge). Hence it seems highly likely that the structure shown in Figure 2 is also the structure found in solution.

Redox Behavior

Cyclic voltammetry was performed on complex $[\mathbf{1}]^{2+}$ in acetonitrile containing 1 M tetrabutylammonium hexafluorophosphate (TBA-PF₆) as the supporting electrolyte (see Figure 3). This evinced an irreversible oxidative process peaking at around +0.7 V (vs. ferrocenium/ferrocene), which we attribute to oxidation of the benzenedithiolate ligands by analogy to the behavior observed for the monomeric species $[\text{Co}^{\text{III}}(\text{bdt})(\text{Me}_2\text{bpy})_2]^{1+}$ in this solvent system (see below).^[28] In terms of reductive elec-

trochemistry, the sample displayed an irreversible wave at –1.4 V, followed by a more reversible wave at around –1.8 V, with this latter value agreeing well with the position of the couple for the reduction of free Me_2bpy in acetonitrile as determined by Saji and Aoyagui.^[29] It seems, therefore, that the reductive process at –1.4 V leads to decomposition of the complex and the consequent liberation of free 5,5'-dimethyl-2,2'-bipyridine. Meanwhile, complex $[\mathbf{1}]^{2+}$ also possesses a reversible wave ($E_{1/2} = -0.63$ V), evident over both the wide and narrow potential windows scanned in Figure 3. Controlled potential electrolysis of this reversible wave at –1.0 V (vs. ferrocenium/ferrocene) indicated that it corresponded to a one-electron redox process (1.44 C were passed, out of a theoretical maximum of 1.53 C for a one-electron process). Hence it appears that this wave may correspond to the reversible reduction (to Co^{II}) and re-oxidation (to Co^{III}) of only one of the two cobalt centers in the complex (vide infra).

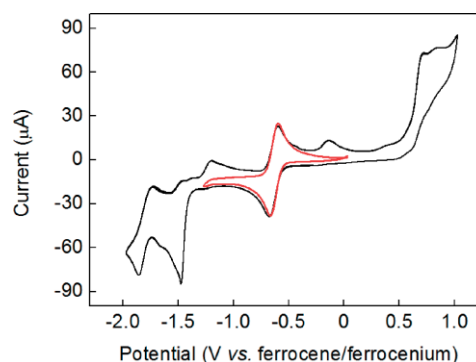


Figure 3. Cyclic voltammogram of a 2.3 mM acetonitrile solution of complex $[\mathbf{1}]^{2+}$ containing 1 M TBA-PF₆ run under the conditions detailed in the Experimental Section. The black trace shows the behavior over the potential range +1 to –2 V vs. reference, and the red trace shows the reversible nature of the one-electron $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ wave over a narrower potential window.

Calculations

In order to elucidate the nature of the species giving rise to the redox waves observed in Figure 3, the electronic structures for this electron transfer series were investigated by DFT calculations. The geometry-optimized structure of $[1]^{2+}$ at the BP86 level of theory revealed average Co–S and Co–N bond lengths of 2.276 Å and 1.973 Å, which are ≈ 0.02 Å and 0.009 Å longer, respectively, than the experimental data (see Table 1, and Figure S3 and Table S1). The optimized structure nicely reproduces the bonding pattern of the first coordination sphere, with the Co2–N4 and Co2–N5 bonds that are *trans* to the bridging sulfur atoms being longer than the other two Co–N bonds about Co2 (Figure 2). Similarly, lengths of the Co1–S bonds to the bridging atoms are about 0.05 Å shorter than the Co1–S2 and Co1–S4 distances, just as seen experimentally. The dimensions of the $\{Co_2S_2\}$ diamond core are also well-reproduced in the optimized structure, with a slight overestimation of the Co...Co separation by 0.08 Å due to a minute expansion of the Co–S–Co angles.

The molecular orbital (MO) manifold presented in Figure 4 for complex $[1]^{2+}$ depicts two octahedral low-spin Co^{III} centers, each with a filled t_{2g} set of orbitals and empty e_g orbitals. The relative energies of these MOs reflects their individual coordination spheres; the d orbital manifold for Co2 is stabilized with respect to Co1 as it has fewer π -donating sulfur ligands. Thus, the e_g MOs of Co2, specifically the $d_{x^2-y^2}$ (where the N3–Co2–N6 vector is defined as the z-axis in this ESBO complex), represent the lowest unoccupied orbitals (LUMO) with more coordinating 2p donor atoms than for Co1. The highest occupied orbitals (HOMO) are ligand-based; specifically, the π_3 orbital of the bdt ligand (Figure 4).^[4,30] This supports the assignment of

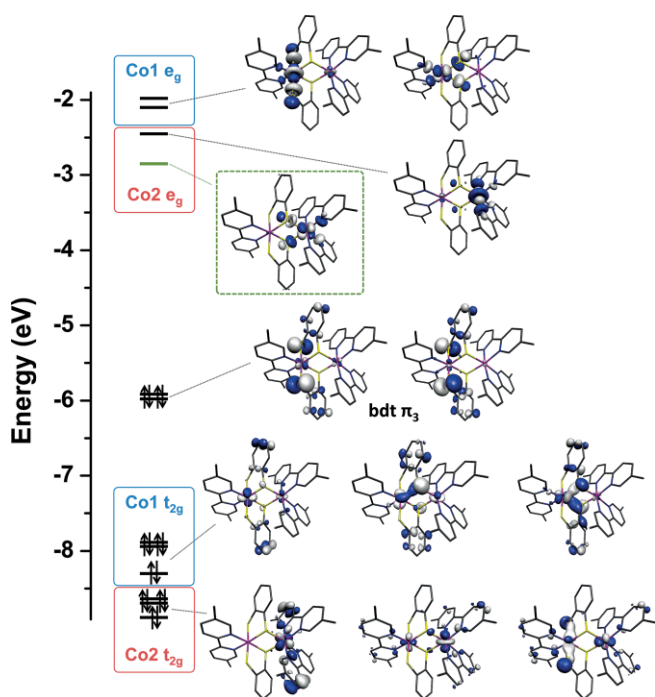


Figure 4. Qualitative MO scheme depicting the ordering of the frontier orbitals for $[1]^{2+}$ showing two low-spin Co^{III} ions, with the LUMO highlighted in the green dashed box.

the oxidation of $[1]^{2+}$ (see Figure 3 and associated discussion) as being ligand-centered, and that the process is irreversible; a bdt radical anion ligand is incapable of bridging two Co^{III} ions, as was also observed with the monocobalt complex.^[28]

Complex $[1]^{2+}$ exhibits a reversible one-electron reduction at -0.63 V (vs. ferrocenium/ferrocene), which was tentatively assigned as metal-centered on account of the mild potential relative to that typically observed for bpy ligands in homoleptic complexes.^[31] This assignment is confirmed by these calculations. The geometry-optimized structure of the one-electron reduced species $[Co_2(bdt)_2(Me_2bpy)_3]^+$ (denoted $[1]^+$) retained the ESBO connectivity (Figure S4 and Table S2). Complex $[1]^+$ is a $Co^{III/II}$ mixed-valence complex where the singly-occupied orbital (SOMO) is the σ^* MO of Co2. The low-spin $S = 1/2$ solution is 12.8 kcal mol⁻¹ more stable than the corresponding high-spin $S = 3/2$ configuration of the Co^{II} ion, a consequence of the relatively strong ligand field comprising bridging thiolate donors and π -accepting Me_2bpy ligands. The Mulliken spin population analysis confirms this compound as class I mixed-valency, given the inequivalence of the Co ions as defined by their respective first coordination spheres (Figure 5).^[32] The reduction of Co2 to a low-spin d^7 ion gives rise to a Jahn–Teller distortion along what is defined as the x-axis, with the elongation of the Co2–S3 and Co2–N4 bond lengths by 0.44 Å and 0.11 Å, respectively (Table 1). The other bonds about Co2 are marginally shorter as expected for a distortion of this type, and those about Co1 remain unchanged. Further reduction of this complex to the neutral species is predicted to sever the Co2–S3 bond, giving square pyramidal and octahedral Co^{II} ions (possibly evinced by the irreversible reductive process at -1.4 V in the cyclic voltammogram in Figure 3).

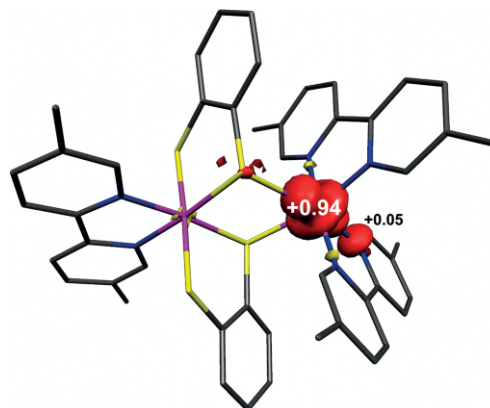


Figure 5. Mulliken spin population analysis for $[1]^+$ (red: α -spin; yellow: β -spin).

The above calculations allow the electronic spectra of complex $[1]^{2+}$ before and after one-electron reduction to be interpreted (see Figure S5). Hence the as-isolated dicobalt(III) form displays two low energy LMCT bands ascribed as $S \rightarrow Co_2$ at 776 nm ($\epsilon = 2200$ M⁻¹ cm⁻¹) and $S \rightarrow Co_1$ at 598 nm ($\epsilon = 2300$ M⁻¹ cm⁻¹).^[12e,33] The latter is the characteristic band seen in many monometallic Co^{III} complexes with sulfur donor ligands.^[28] The shift to lower energy for the $S \rightarrow Co_2$ band stems from the stabilization of the e_g orbitals of Co2 by the two Me_2bpy ligands (Figure 4). After reduction by one electron, a

new "sharp" peak appears at about 650 nm, which is assigned as $S \rightarrow \text{Co}2$ LMCT as previously reported in mixed-valence $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ species,^[34] and which sits adjacent to the $S \rightarrow \text{Co}1$ LMCT that is retained in the one-electron reduced complex.

Conclusions

In summary, we have presented the first known example of a mixed diimine/dithiolate dicobalt complex where the two cobalt centers are in dissimilar coordination environments (complex $[\mathbf{1}]^{2+}$). The structure of complex $[\mathbf{1}]^{2+}$ was determined by single-crystal X-ray diffraction studies, whilst NMR and mass spectrometry data imply that this structure is maintained in solution. The different coordination environments around the two cobalt centers then cause these two centers to have differing redox activity, as shown by the experimental electrochemical analyses. Finally, DFT calculations on complex $[\mathbf{1}]^{2+}$ and its one-electron reduced analog (complex $[\mathbf{1}]^+$) help to rationalize the redox behavior observed by cyclic voltammetry, and show that the metal center coordinated to two diimine units is the easier of the centers to reduce, with subsequent reduction of the second cobalt center leading to irreversible decomposition of the complex.

Experimental Section

General Experimental Remarks: All solvents were obtained from Sigma Aldrich and used as supplied. 5,5'-dimethyl-2,2'-bipyridine (98 %), *o*-benzenedithiol (96 %), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98 %) and tetrabutylammonium hexafluorophosphate (TBA-PF₆) (99 %) were supplied by Sigma Aldrich.

All ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 300 K. Chemical shifts are reported in parts per million from low to high field. Coupling constants (*J*) are reported in Hertz [Hz]. Standard abbreviations indicating multiplicity were used as follows: m = multiplet, d = doublet, s = singlet. UV/Vis spectra were recorded on a JASCO V-670 spectrophotometer using 1 cm path length cuvettes. CHN analyses were collected by the services facility at the School of Chemistry, University of Glasgow, as were LM-MS mass spectra (ESI, positive mode, Bruker micrOTOF-Q machine). IR spectra were collected in the solid state on a Shimadzu IRAffinity-15 Fourier Transform Infrared Spectrophotometer. Experiments performed at "room temperature" were carried out at 20 °C. Electrochemical experiments were performed as below.

[Co^{III}₂(bdt)₂(Me₂bpy)₃](NO₃)₂, $[\mathbf{1}](\text{NO}_3)_2$: To a solution of 5,5'-dimethyl-2,2'-bipyridine (0.640 g, 3.48 mmol, 2 equiv.) in methanol (20 mL) under air was added a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.508 g, 1.74 mmol, 1 equiv.) in methanol (10 mL). To this was added a solution of *o*-benzenedithiol (0.248 g, 1.74 mmol, 1 equiv.) in 10 mL of methanol. The reaction mixture was observed to turn dark green upon addition of the dithiol. After stirring in air for 1 h, the solvent was removed under reduced pressure and the resulting solid re-dissolved in 10 mL of MeOH. Around 25 mL of diethyl ether were then added, inducing the formation of a dark green precipitate and a dark brown supernatant solution. This dark green precipitate was isolated by filtration and then re-dissolved in 15 mL of MeOH. To this dark green solution was then added 50 mL of diethyl ether, yielding pure compound $[\mathbf{1}](\text{NO}_3)_2$ as a green microcrystalline solid. This was carefully dried at 150 °C overnight to give a final anhydrous

mass yield of 0.385 g (41 %). Complex $[\mathbf{1}](\text{NO}_3)_2$ is somewhat hygroscopic and hence absorbs water when exposed to laboratory air. Indeed, a sample of dry mass 364 mg was found to increase in mass by 25 mg after standing in air for 1 d (upon further standing the mass did not increase further). This corresponds to a mass-gain of around 6 %, corresponding to around 3.5 molecules of H₂O per formula unit of $[\mathbf{1}](\text{NO}_3)_2$. CHN analysis was then performed on this hydrated sample: C₄₈H₄₄Co₂N₈O₆S₄·(3.5H₂O): calcd. C 50.66, H 4.52, N 9.85; found C 50.61, H 4.40, N 10.35. Yields are calculated from the dry (anhydrous) mass. ¹H NMR (MeOD, 400 MHz): δ = 10.34–10.32 (m, 2 H, H_a or H_i or H_p), 8.44–8.40 (m, 2 H, H_a or H_i or H_p), 8.38 (d, *J* = 8.2 Hz, 2 H, H_d or H_l or H_m), 8.29 (d, *J* = 8.3 Hz, 2 H, H_d or H_l or H_m), 8.08–8.03 (m, 2 H, H_c or H_k or H_n), 8.02–7.91 (m, 6 H, H_d or H_l or H_m and H_c and/or H_k and/or H_n), 7.38–7.34 (m, 2 H, H_a or H_i or H_p), 6.92–6.86 (m, 2 H, H_e or H_f or H_g or H_h), 6.60 (dd, *J*₁ = 8.0, *J*₂ = 0.8 Hz, 2 H, H_e or H_f or H_g or H_h), 6.56–6.50 (m, 2 H, H_e or H_f or H_g or H_h), 6.03 (dd, *J*₁ = 7.8, *J*₂ = 0.9 Hz, 2 H, H_e or H_f or H_g or H_h), 2.67 (s, 6 H, H_b or H_j or H_o), 2.29 (s, 6 H, H_b or H_j or H_o), 2.26 (s, 6 H, H_b or H_j or H_o) ppm. Assignments of signals to groups of protons are based on 2D (COSY) spectra and the expected coupling patterns of the peaks, although the symmetry of the molecule prevents unambiguous assignments. Letter codes correspond to those shown in Scheme 1. The ¹H NMR spectrum of this compound is shown in the Supporting Information (Figures S1 and S2). ¹³C NMR (MeOD, 400 MHz): δ = 159.5, 156.0, 155.9, 155.0, 153.1, 151.7, 149.2, 143.2, 142.8, 141.2, 140.7, 138.7, 138.5, 132.7, 132.4, 130.6, 129.8, 125.4, 125.1, 124.8, 123.2, 19.5, 18.9, 18.6 ppm. IR (solid state): $\tilde{\nu}$ = 3041 (w), 1473 (w), 1432 (w), 1331 (s), 1236 (m), 825 (m), 734 (m) cm⁻¹. ESI-LMMS (methanol): *m/z* = 475.0508 $[\mathbf{M}]^{2+}$ (calcd. for C₄₈H₄₄Co₂N₈S₄; 475.0587).

Electrochemical Methods: Electrochemical studies were performed in a single chamber cell in a three-electrode configuration using a CH Instruments CHI700 series potentiostat. The supporting electrolyte was 1 M TBA-PF₆ in acetonitrile, unless otherwise noted. A Pt wire was used as the counter electrode, along with an Ag/AgNO₃ pseudo reference electrode. Potentials are reported relative to the ferrocenium/ferrocene couple, the position of which was judged by adding ferrocene to the samples analyzed. Working electrodes were washed with acetone and deionized water prior to use. Cyclic voltammograms were collected at room temperature under an atmosphere of Ar at a scan rate of 100 mV s⁻¹. A glassy carbon button electrode (area = 0.071 cm², CH Instruments) was used as the working electrode for cyclic voltammetry. Measurements were conducted without stirring and with *iR* compensation enabled. Bulk electrolyses were carried out in 0.1 M TBA-PF₆ in acetonitrile in a two-chamber cell, using an Ag/AgNO₃ pseudo reference electrode, a large area carbon felt counter electrode and a large area carbon felt working electrode. Solutions were stirred during bulk electrolysis.

Calculations: The program package ORCA was used for all calculations.^[35] The geometries of all molecules were fully optimized by a spin-unrestricted DFT method employing the BP86 functional with acetonitrile as the solvent.^[36] Triple- ξ -quality basis sets with one set of polarization functions (def2-TZVP) were used for all atoms.^[37] The single-point calculations were performed with the PBE0^[38] functional on optimized and crystallographic coordinates using the same basis sets and enhanced integration accuracy for metal atoms (SPECIALGRIDINTACC 10). A scalar relativistic correction was applied using the zeroth-order regular approximation (ZORA) method.^[39] The RIJCOSX approximation^[40] combined with the appropriate Ahlrichs auxiliary basis set was used to speed up the calculations.^[41] The conductor-like screening model (COSMO) was used for all calculations.^[42] The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry con-

straints. The self-consistent field calculations were tightly converged ($1 \times 10^{-8} E_h$ in energy, $1 \times 10^{-7} E_h$ in charge density, and 1×10^{-7} in the maximum element of the DIIS^[43] error vector). The geometry was converged with the following convergence criteria: change in energy $< 10^{-5} E_h$, average force $< 5 \times 10^{-4} E_h \text{ Bohr}^{-1}$, and the maximum force $10^{-4} E_h \text{ Bohr}^{-1}$. The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints. The stability of all solutions was checked by performing frequency calculations: No negative frequencies were observed. Molecular orbitals and spin density maps were visualized via the program Molekel.^[44]

Crystallography

Crystallographic data were collected at the EPSRC UK National Crystallography Service at the University of Southampton using a rotating anode radiation source.^[45] A dark blue/green opaque crystal of dimensions $0.10 \times 0.09 \times 0.02 \text{ mm}$ was used for single-crystal X-ray diffraction data collection. $\text{C}_{48}\text{H}_{44}\text{Co}_2\text{N}_6\text{S}_4 \cdot 2(\text{NO}_3) \cdot 1.25(\text{H}_2\text{O}) \cdot 0.25(\text{CH}_3\text{OH})$ crystallized in the monoclinic space group $P2_1/n$ (space group No. 14), with unit cell dimensions $a = 12.6021(3) \text{ \AA}$, $b = 22.7893(5) \text{ \AA}$, $c = 17.1872(6) \text{ \AA}$, $\beta = 103.500(3)^\circ$ and $V = 4799.7(2) \text{ \AA}^3$, $T = 100 \text{ K}$. 59216 reflections were measured by ω scans, 11002 independent reflections with $R_{\text{int}} = 0.053$, $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.4^\circ$ using Mo- K_{α} radiation, $\lambda = 0.71073 \text{ \AA}$, on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC10 goniometer and HG Saturn 724+ detector diffractometer. Data were integrated using *CrysAlis PRO* 1.171.38.43 (Rigaku OD, 2015), with Lorentz and polarization corrections made. A multi-scan correction for absorption was applied $T_{\text{min}} = 0.538$, $T_{\text{max}} = 1.000$, $\mu = 0.93 \text{ mm}^{-1}$, $M_r = 1105.54$, $F(000) = 2284$, $\rho_{\text{calcd.}} = 1.530 \text{ Mg m}^{-3}$.

The structure was solved using ShelXT.^[46] All 11002 reflections were used in the refinement and positions and anisotropic atomic displacement parameters (adps) were refined for all fully occupied non-hydrogen atoms using SHELXL within OLEX2.^[47,48] A region of lattice solvent was modelled as $0.75\text{H}_2\text{O}$ with two further 0.25-occupied H_2O molecules and a 0.25-occupied molecule of MeOH. One nitrate anion was modelled with the oxygen atoms over two partially occupied (0.9/0.1) sites. The 0.75-occupied H_2O hydrogen atoms were located in difference Fourier maps and refined with O-H distance restraints, hydrogen atoms for the 0.25- H_2O and MeOH were not included in the model but were included in the unit cell contents and values derived from them, otherwise hydrogen atoms were placed in calculated positions and refined as part of a riding model or as a rigid rotor for Me hydrogen atoms. Final $wR(F^2) = 0.097$, $R[F^2 > 2\sigma(F^2)] = 0.043$ [8780 reflections with $I > 2\sigma(I)$] for 670 parameters, $\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$ and $\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$ maximum and minimum residual electron density.

CCDC 1537318 [for $[\mathbf{1}](\text{NO}_3)_2$] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): ^1H NMR and UV/Vis spectra of compound $[\mathbf{1}](\text{NO}_3)_2$, additional computational and crystallographic data.

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