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 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. Within this class of compounds, multimetallic complexes containing dithiolene ligands show particular promise for the development of new materials with exciting properties. 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 [M₂(dithiolene)₂] (M = Mn, Fe, Co, Ni), [M₂(dithiolene)₃] (M = Mo, Rh, Re) and [M₂(Cp)₂(dithiolene)₂] (Cp = cyclopentadienyl, M = V, Cr, Fe, Co, Mo, Rh). 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, whereby aerial oxidation of the monomeric complex [Ni(bdt)(bpy)] in DMF leads to the generation of mixtures of [(bpy)₂Ni(bdtO₂)Ni(bdt)] and [(bpy)₂Ni(bdtO₄)Ni(bdt)] (bpy = 2,2′-bipyridine, bdt⁻ = 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.

Meanwhile, Wacholtz, Mague, and co-workers have reported two allied tri-zinc complexes where one zinc center is coordinated to 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. 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...
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 dithiolens, 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 \([\text{Co}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3]^{2+}\) 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 \([\text{1}]^{2+}\) indicates that it undergoes a reversible one-electron reduction reaction at very modest cathodic potentials, producing a mixed-valence CoIIICoII species, the likely nature of which we have rationalized using computational methods.

Results and Discussion

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

A general route to the synthesis of dicobalt complex \([\text{1}]^{2+}\) is given in Scheme 1. Hence, addition of one equivalent of \(\text{Co(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}\) to two equivalents of \(5,5'-\text{dimethyl}-2,2'-\text{bipyridine (Me}_2\text{bpy)}\) 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 \(\text{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 \([\text{1}]\text{(NO}_3\text{)}_2\) suitable for X-ray diffraction (Figure 2).

The connectivity of \([\text{1}]^{2+}\) 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 bond lengths in Figure 2 are Co1–S1 = 2.2222(7) Å, Co1–S2 = 2.2688(7) Å, Co1–S3 = 2.2251(8) Å, Co1–S4 = 2.2709(8) Å, Co2–S1 = 2.2663(8) Å and 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 \([\text{Co(Tab)}_2(4,4'-\text{dmbpy})_2]\text{(PF}_6\text{)}_3\), where Tab is \(4-(\text{trimethylammonio})\text{benzenethiolate and 4,4'-dmbpy is 4,4'-dimethylbipyridine.}\[20\] Most of the angles around Co2 are within the range 85 < \(\theta\) < 95°, 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 Co2 are within the range 85 < \(\theta\) < 95°, 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 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 \([\text{Co}_2X_2]\) 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 \(\text{OH}^-/\text{NH}_2^-\)-bridged\[27\] to

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

Figure 2. The molecular structure of the di-cationic complex in crystals of \([\text{Co}_2(\text{bdt})_2(\text{Me}_2\text{bpy})_3]\text{(NO}_3\text{)}_2\). 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.
Table 1. Experimental and calculated bond lengths [Å] and angles [°] in [Co₂(bdt)₂(Me₂bpy)₃]⁺ (z = 2+, 1+).

<table>
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<th></th>
<th>[Co₁⁻Ι⁻(bdt)₂(Me₂bpy)₃]²⁺</th>
<th>calcld.</th>
<th>[Co₁⁻Ι⁻(bdt)₂(Me₂bpy)₃]¹⁺</th>
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3.35(1)–3.3441(2) Å with the larger thiolato ligands. Akin to other bimetallic complexes with five chelating ligands, the chirality about each Co center in [1]²⁺ is the same (ΛΛ) for each tris-chelate Co ion. The only exception to this rule for bimetallic complexes with five chelating ligands is [Co₂(Et₂dtc)₅]¹⁺ ([Et₂dtc]⁻ = diethyldithiocarbamato), where the each Co center has an opposing chirality.

The solution-phase ¹H NMR of complex [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 [CoⅢ(bdt)(Me₂bpy)]⁺, whilst the unique bipyridine coordinated to Co1 sits in a more symmetrical chemical environment.

Redox Behavior

Cyclic voltammetry was performed on complex [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 [CoⅢ(bdt)(Me₂bpy)]⁺ in this solvent system (see below). In terms of reductive electrochemistry, 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 Me₂bpy in acetonitrile as determined by Saji and Aoyagui. 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 [1]²⁺ also possesses a reversible wave (E₁/₂ = –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 CoⅡ) and re-oxidation (to CoⅢ) of only one of the two cobalt centers in the complex (vide infra).
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–S4 and Co1–S5 distances, just as seen experimentally. The dimensions of the [Co2S2] diamond core are also well-reproduced in the optimized structure, with a slight overestimation of the Co–S distances, just as seen experimentally. The dimensions of the [Co2S2] diamond core are also well-reproduced in the optimized structure, with a slight overestimation of the Co–S–Co angles. The molecular orbital (MO) manifold presented in Figure 4 for complex $[1]^{2+}$ depicts two octahedral low-spin CoIII centers, each with a filled t2g set of orbitals and empty eg 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 eg MOs of Co2, specifically the dπ2–y2 (where the N3–Co2–N4 bond 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 πσ orbital of the bdt ligand (Figure 4).[23] This supports the assignment of 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 CoII 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 [Co2(bdt)2(Me2bpy)]+ (denoted $[1]^{-}$) retained the ESBO connectivity (Figure S4 and Table S2). Complex $[1]^{-}$ is a CoIII(bpy) mixed-valency complex where the singly-occupied orbital (SOMO) is the π* 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 CoII ion, a consequence of the relative strong ligand field comprising bridging thiolate donors and π-accepting Me2bpy 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 S5).[32] The reduction of Co2 to a low-spin d7 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 CoII ions (possibly evinced by the irreversible reductive process at −1.4 V in the cyclic voltammogram in Figure 3).
new “sharp” peak appears at about 650 nm, which is assigned as $S \rightarrow Co^{2+}$ LMCT as previously reported in mixed-valence Co$^{III}$/Co$^{I}$ species, and which sits adjacent to the $S \rightarrow Co^{1+}$ 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 1$^{2+}$). The structure of complex 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 1$^{2+}$ and its one-electron reduced analog (complex 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 %), Co(NO$_3$)$_2$·6H$_2$O (98 %) and tetra-butylammonium hexafluorophosphate (TBA-PF$_6$) (99 %) were supplied by Sigma Aldrich.

All $^1$H and $^{13}$C 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 cuvets. CHN analyses were performed at “room temperature” on a Shimadzu IRAffinity-1S Fourier Transform Infrared Spectrophotometer. Experiments performed at “room temperature” were carried out at 20 °C.

**Calculations:**

**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-PF$_6$ in acetonitrile, unless otherwise noted. A Pt wire was used as the counter electrode, along with an Ag/AgNO$_3$ 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 cm$^2$) 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-PF$_6$ in acetonitrile in a two-chamber cell, using an Ag/AgNO$_3$ pseudo reference electrode, a large area carbon felt counter electrode and a large area carbon felt working electrode. Solutions were stirred during bulk electrolysis.

Formulations of all molecules were fully optimized by the B3LYP functional with the 6-31G(d) basis set and enhanced integration accuracy for metal atoms (SMD) at 0 K.

**Calculations:** The program package ORCA was used for all calculations. The geometries of all molecules were fully optimized by a spin-unrestricted DFT method employing the B3LYP functional with the 6-311+G(d,p) basis set.

**Calculations:** The RIJCOX approximation combined with the appropriate Ahlrichs auxiliary basis set was used to speed up the calculations.

**Calculations:** The conductor-like screening model (COSMO) was used for all calculations.

**Calculations:** The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry con-
strains. The self-consistent field calculations were tightly converged (1 × 10⁻⁸ Eh in energy, 1 × 10⁻⁷ Eh 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 direction for absorption was applied. Placement parameters (adps) were refined for all fully occupied (0.9/0.1) sites. The 0.75-occupied H₂O hydrogen atoms were placed in calculated positions and refined as a riding model or as a rigid rotor for Me hydrogen atoms. Final 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 × 0.09 × 0.02 mm was used for single-crystal X-ray diffraction data collection. C₅₈H₉₄Co₂N₆S₄(NO₃)₂·1.25(H₂O)·0.25(CH₃OH) crystallized in the monoclinic space group P2₁/a (space group No. 14), with unit cell dimensions a = 12.6021(3) Å, b = 22.7893(5) Å, c = 17.1872(6) Å, β = 103.500(3)° and V = 4799.7(2) Å³, T = 100 K. 59216 measurements were collected by 8ω scans, 11002 independent reflections with Rint = 0.053, Tmin = 27.5°, θmin = 2.4° using Mo-Kα radiation, λ = 0.71073 Å, on a Rigaku FRED+ equipped with VHF Varimax confocal mirrors and an AFC10 goniometer and HG Saturn 72+ detector diffractometer. Data were integrated using CrystAlis PRO 1.171.3843 (Rigaku OD, 2015), with Lorentz and polarization corrections made. A multi-scan correction for absorption was applied w = 0.538, T = 1000, μ = 0.93 mm⁻¹, M = 1105.54, F(000) = 2284, ρcalcd = 1.530 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 0.75H₂O with two further 0.25-occupied H₂O molecules and a 0.25-occupied molecule of MeOH. One nitrate anion was modelled with the oxygen atoms over two partial occupied (0.9/0.1) sites. The 0.75-occupied H₂O hydrogen atoms were located in difference Fourier maps and refined with O-H distance restraints, hydrogen atoms for the 0.25-H₂O 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 wR²(F²) = 0.097, R[F² > 2σ(F²)] = 0.043 [8780 reflections with l > 2σ(l)] for 670 parameters, Δρmax = 0.50 e Å⁻³ and Δρmin = −0.39 e Å⁻³ maximum and minimum residual electron density. CCDC 1537318 for [1][NO₃]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 [1][NO₃]₂, additional computational and crystallographic data.

Acknowledgments

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Keywords: Cobalt · Coordination modes · Dithiolate ligands · Redox chemistry · Density functional calculations