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The molecular and electronic structures of monomeric cobalt complexes containing redox noninnocent *o*-aminobenzenethiolate ligands

Stephen Sproules, Ruta R. Kapre, Nabarun Roy, Thomas Weyhermüller, Karl Wieghardt*

Max-Planck-Institut für Bioanorganische Chemie, Stiftstrasse 34-36, D-45470 Mülheim an der Ruhr, Germany

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ABSTRACT

Dark blue $[PPh_4][Co^{III}(^2L)]$ (2), where $(^2L)^{2-}$ represents the closed-shell dianion of 4,6-di-*tert*-butyl-2-[(pentafluorophenyl)amino]benzenethiol, has been synthesized from the reaction of $H_2(^2L)$ and CoCl₂ (2:1) in acetonitrile with excess NEt₃, brief exposure of the solution to air, and addition of $[PPh_4]Br$. The oxidation of **2** with one equivalent of iodine produces the neutral species $[Co^{III}(^{2}L)_{2}I]^{0}$ (**3**), where $(^{2}L)^{1-}$ represents the one-electron oxidized π radical anion of $(^{2}L)^{2-}$. Crystalline [Co^{III}(⁴L)] (**4**), where $({}^{4}L')^{3-}$ is the π radical monoanion of bis-2,2'-(1,2-diphenylethylenediimine)-benzenethiolate, was precipitated from a toluene reflux of $[Co^{II}({}^{3}L)_{2}]$, where $({}^{3}L)^{2-}$ is the closed-shell monoanion of 2-(phenylmethylamino)benzenethiol. The reduction of 4 with CoCp₂ under anaerobic conditions yielded dark violet crystals of [CoCp₂][Co^{III}(⁴L)] (5). The reaction of Zn(CH₃CO₂)₂ with 2-phenylbenzothiazoline in methanol resulted in the formation of $[Zn^{II}(^{3}L)_{2}]^{0}$ (6). The two monoanions 2, and 5, along with $[N(n-Bu)_{4}][Co(abt)_{2}]$ (1) $(abt^{2-} = o$ -aminobenzenethiolate), and neutral **4** have all been shown by X-ray crystallography to be square planar. A tetrahedral geometry was adopted by 6. From temperature dependent (3–300 K) magnetic susceptibility measurements, it was established the monoanions have a triplet ground state characterized by a large zero field splitting. EPR measurements of 4, and electrochemically oxidized 1 and 2 reveal distinctly different spin Hamiltonian parameters that are interpreted with the aid of density function theoretical (DFT) calculations. It is shown that oxidation states describing a d^6 Co(III) or d^7 Co(II) cannot be unambiguously assigned for these neutral and monoanionic species.

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1. Introduction

The evaluation of the correct valence electron count for a given transition metal coordination compound is an important task for the understanding and prediction of its spectroscopic properties and or its reactivity. Perhaps the most effective means of accounting for electrons is the concept of an oxidation state. A formal oxidation state of any given metal ion is a nonmeasurable integer which is commonly defined as "the charge left on the metal after all the ligands have been removed in their closed-shell form" [1]. The distinction is made with a physical or spectroscopic oxidation state, a value derived from a known dⁿ configuration that is measurable quantity determined by various spectroscopic and theoretical techniques [2]. In many cases, the formal and physical oxidation states are identical. However, they differ if one of the ligands in the complex is an open-shell organic radical [3]. These radical ligand metal ion complexes, M-L, constitute a rapidly growing class of coordination compounds. Identification of such a bonding situation experimentally has been improved by involving a combination of spectroscopic, crystallographic and theoretical techniques [3–5], that facilitate a physical oxidation state assignment to the metal (and ligand).

While there is no impediment to assigning a formal oxidation state, there are limits to successfully defining a physical oxidation state, and in the vast array of characterized coordination compounds of the first row transition metals, cobalt complexes are perhaps the most demanding [6–9]. Several recent studies have shown that the bonding arrangement in four-coordinate complexes of cobalt with two noninnocent ligands cannot be simply described using integer oxidation levels for the metal and ligands because the energy of the cobalt 3d orbitals is comparable to the ligand π orbitals [5,6,9].

Herein, we present the coordination chemistry of cobalt complexes chelated by aminobenzenethiolate ligands (Scheme 1). They can exist at four distinctly different protonation and oxidation levels [10,11]; the structural parameters associated with these states are shown in Scheme 2. Birker et al. reported the isolation of a monomeric complex with two unsubstituted *o*-aminobenzenethiolate(2–) ligands, $(abt)^{2-}$, bound to cobalt, $[N(n-Bu)_4][Co(abt)_2]$ (1) [12]. It was shown to have an *S* = 1 ground state, however, this compound had not been structurally characterized. Therefore, we report its crystal structure along with the structure of $[PPh_4]$ - $[Co^{III}(^2L)_2]$ (2), where $(^2L)^{2-}$ represents the sterically encumbered

^{*} Corresponding author. *E-mail address:* wieghardt@mpi-muelheim.mpg.de (K. Wieghardt).

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Ligands



4,6-di-*tert*-butyl-2-[(2-pentafluorophenyl)-amino]benzenethiolate(2–) ligand [11]. We have also prepared the complex $[Co^{III}(^{2}L)_{2}I]$ (**3**) from the oxidation of the parent monoanion with molecular iodine.

Tetradentate bis-2,2'-(1,2-diphenylethylenediimine)benzenethiolato(4-), (⁴L)⁴⁻, is formed via a carbon-carbon bond formation from two 2-(phenylmethyleneamino)benzenethiolate(1-) units, (³L)^{1–}, while coordinated to either a nickel or cobalt transition metal ion (Scheme 3) [13]. The presence of bulky aromatic substituents ensured the isolation of a monomeric charge neutral [Co^{III}(⁴L[•])] (**4**). High-quality X-ray crystallography at cryogenic temperatures for this and its one-electron reduced monoanion. [CoCp₂][Co^{III}(⁴L)] (**5**) provide a means of determining whether this redox event is metal- or ligand-centered. Finally, Kochin et al. reported formation of [Zn^{II}(⁴L^{..})] from the reaction of 2-phenylbenzothiazoline with zinc acetate [14]. However, when the reduction of the alkane bridge with sodium borohydride failed - a technique partially successful for nickel analogue [15] - the formulation of this species was doubtful. We show here the compound is actually



 $[Zn^{II}({}^{3}L)_{2}]$ (**6**) as confirmed by a X-ray crystallographic analysis. Throughout this work, we will describe these compounds based on the *most favored* electronic structure as preferred by the experimental data, despite the ambiguity in assigning an oxidation state for the central cobalt ion.

2. Experimental section

2.1. Synthesis of complexes

All manipulations were carried out with standard Schlenk line and glove box techniques. Synthesis of the ligand 4,6-di-*tert*-2-[(pentafluorophenyl)amino]benzenethiol, $H_2(^2L)$ has been described in Ref. [11]. The compounds [N(*n*-Bu)₄][Co^{III}(abt)₂] (1) [12], [Co^{II}(³L)₂] [13], and [Co^{III}(⁴L)] (4) [13] have all be prepared according to published procedures.

2.2. $[PPh_4][Co^{III}(^2L)_2]$ (2)

The ligand $H_2(^{2}L)$ (0.60 g; 1.50 mmol) was dissolved in dry acetonitrile (15 cm³) under anaerobic conditions. To this yellow solution was added CoCl₂ (96 mg; 0.75 mmol) and triethylamine (0.40 cm³; 3.0 mmol) and the reaction mixture was stirred under Ar for 15 min. Upon limited exposure to air, the green solution became dark blue, after which the acetonitrile was removed under vacuum and replaced by dichloromethane (20 cm³). Tetraphenylphosphonium bromide, [PPh₄]Br (0.30 g; 0.75 mmol) was added under anaerobic conditions (glovebox) and the mixture stirred for another 15 min. before filtering through Celite. The volume of the filtrate was reduced to 5 cm^3 and *n*-hexane (25 cm^3) was added to afford a blue precipitate of 1. The powder was separated by filtration and stored under an inert atmosphere. Single crystals suitable for X-ray diffraction study were grown by slow diffusion of diethyl ether into a dichloromethane solution of the product yielding 1 Et₂O. Yield: 0.60 g (79%).

Anal. Calc. for $C_{64}H_{60}N_2F_{10}PS_2Co: C, 63.99$; H, 5.03; N, 2.33; Co, 4.61. Found: C, 64.06; H, 5.12; N, 2.46; Co, 4.96%. Electrospray ionization (ESI) mass spectrum (CH₂Cl₂, neg. ion mode): m/z = 860.2 [CoL₂]⁻.

2.3. $[Co^{III}(^{2}L^{\cdot})_{2}I]$ (3)

The complex $[PPh_4][Co(^2L)_2]$ (2) (0.08 g; 0.07 mmol) was dissolved in dry dichloromethane (15 cm³) under anaerobic condi-



Scheme 3. Synthesis of $[M({}^{3}L)_{2}]$ and $[M({}^{4}L)]$.

tions. To this dark blue solution was added I_2 (0.02 g; 0.18 mmol) dissolved in *n*-hexane (15 cm³) and stirred for 20 min. The solvent was then removed in vacuo, the residue reconstituted in diethyl ether and filtered through Celite. Evaporation of the solvent under reduced pressure yielded the product as a green black microcrystalline solid. Yield: 0.05 g (56%).

Anal. Calc. for $C_{40}H_{40}N_2F_{10}S_2$ Col: C, 48.59; H, 4.07; N, 2.84; Co, 5.96; I, 12.83. Found: C, 48.41; H, 3.88; N, 2.86; Co, 5.66; I, 13.06%. ESI mass spectrum (CH₂Cl₂, neg. ion mode): m/z = 860.9 [M–I][–].

2.4. [Co^{III}(⁴L[•])] (**4**)

A suspension of $[Co^{II}({}^{3}L)_{2}]$ [13] (0.22 g; 0.45 mmol) in toluene (15 cm³) was heated for 30 min. The dark teal solution was filtered and the solvent removed by rotary evaporation. The dark blue residue was reconstituted in dichloromethane, filtered, then eluted on a silica gel (230–400 mesh) chromatography column using dichloromethane as eluent. The first dark blue band was collected and removal of the solvent under reduced pressure yielded **4** as a metallic aubergine microcrystalline solid. Yield: 0.11 g (50%).

Anal. Calc. for $C_{26}H_{20}N_2S_2Co$: C, 64.58; H, 4.17; N, 5.80; Co, 12.25. Found: C, 64.4; H, 4.1; N, 5.6; Co, 12.2%.

2.5. [CoCp₂][Co^{III}(⁴L)] (**5**)

To a deep blue solution of **4** (0.24 g; 0.50 mmol) in dichloromethane (25 cm³) under an Ar atmosphere was added cobaltocene (95 mg; 0.50 mmol). After the solution was stirred at ambient temperature for 1 h, the violet precipitate that emerged was isolated by filtration. Single crystals suitable for diffraction analysis were grown by slow evaporation of the compound dissolved in a 1:1 mixture of acetonitrile/methanol. Yield: 0.26 g (80%).

Anal. Calc. for C₃₆H₃₀N₂S₂Co₂: C, 64.29; H, 4.46; N, 4.17. Found: C, 64.2; H, 4.4; N, 4.2%.

2.6. $[Zn^{II}({}^{3}L)_{2}]$ (**6**)

Zinc acetate (1.1 g; 5.0 mmol) was added to refluxing solution of 2-phenylbenzothiazoline (2.1 g; 10.0 mmol) in methanol (50 cm³). After stirring for 30 min, an orange precipitate was collected by filtration and washed with methanol, then diethyl ether. X-ray quality single crystals of **6** were obtained by slow evaporation of a dichloromethane/methanol solution of the complex. Yield: 1.7 g (70%).

Anal. Calc. for C₂₆H₂₀N₂S₂Zn: C, 63.68; H, 4.08; N, 5.71. Found: C, 63.7; H, 4.2; N, 5.8%.

2.7. X-ray crystallographic data collection and refinement of the structures

Single crystals of compounds 1, 2 Et₂O, 4, 5 0.5MeCN, and 6 were coated with perfluoropolyether, picked up with nylon loops and were immediately mounted in the nitrogen cold stream of a Bruker-Nonius KappaCCD diffractometer equipped with a Mo-target rotating-anode X-ray source. Graphite monochromated Mo Ka radiation (λ = 0.71073 Å) was used throughout. Final cell constants were obtained from least squares fits of all measured reflections. Intensity data were corrected for absorption using intensities of redundant reflections using sADABS [16]. The structures were readily solved by Patterson methods and subsequent difference Fourier techniques. The Siemens ShelXTL [17] software package was used for solution and artwork of the structures. SHELXL97 [18] was used for the refinement. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters, except for some methyl-hydrogen atoms in disordered acetonitrile molecules of crystallization, which could not be reliably located. Crystallographic data of the compounds are listed in Table 1.

A phenyl ring in the $[PPh_4]^+$ cation (C81–C86), and a diethylether molecule of crystallization (O100–C104) in **2** were found to be disordered. A split atom model was refined giving an occupation ratio of about 0.53:0.47. SAME, EADP and SADI restraints of SHELxL97 were used for the refinement.

An ill defined acetonitrile molecule was detected to be disordered next to a crystallographic inversion center in **5**. A split atom model with constrained bond distances using the DFIX instruction of ShelXL was refined. Hydrogen atom positions could not be located for this molecule.

2.8. Physical measurements

Electronic absorption spectra of complexes from the spectroelectrochemical measurements were recorded on a HP 8452A diode array spectrophotometer (200-1100 nm). Cvclic voltammograms were recorded with an EG&G potentiostat/galvanostat. Variable temperature (3-300 K) magnetization data were recorded in a 1 T magnetic field on a SQUID magnetometer (MPMS Quantum Design). Multiple-field variable temperature measurements were done at three different fields (1, 4, and 7 T) for which the magnetization was equidistantly sampled on a 1/T temperature scale. The experimental magnetic susceptibility data were corrected for underlying diamagnetism using tabulated Pascal's constants. X-band EPR spectra were recorded on a Bruker ELEXSYS E500 spectrometer and simulated with XSophe distributed by Bruker Biospin GmbH [19]. Elemental analyses were performed by H. Kolbe at the Mikroanalytischen Labor in Mülheim an der Ruhr, Germany.

2.9. Calculations

All DFT calculations were performed with the ORCA program [20]. The complexes were geometry optimized using the BP86 functional [21]. Scalar relativistic effects have been included using the ZORA method [22]. Since these species are monoanions, or neutral complexes generated in solution, the conductor-like screening model (COSMO) was applied using CH_2Cl_2 as the solvent [23]. The all-electron basis sets were those reported by the Ahlrichs group [24,25]. Triple- ξ -quality basis sets with one set of polarization functions (TZVP) were used for the cobalt and the coordinating oxygen, nitrogen and sulfur atoms. The remaining atoms were described by slightly smaller polarized split-valence SV(P) basis sets that are double- ξ -quality in the va-

Table 1	
Crystallographic data for 1, 2 · Et ₂ O, 4, 5 · 0.5 MeCN, a	and 6 .

	1	$2 \cdot Et_2O$	4	5 ·0.5MeCN	6
Chemical formula	$C_{28}H_{46}N_3S_2Co$	C ₆₈ H ₇₀ F ₁₀ N ₂ OPS ₂ Co	$C_{26}H_{20}N_2S_2Co$	C ₃₇ H _{31.5} N _{2.5} S ₂ Co	$C_{26}H_{20}N_2S_2Zn$
Formula weight (F_w)	547.73	1275.28	483.49	693.13	489.93
Space group	<i>P</i> 2 ₁ / <i>n</i> , No. 14	<i>P</i> 1, No. 2	$P2_1/n$, No. 14	$P2_1/n$, No. 14	<i>P</i> 2 ₁ / <i>n</i> , No. 14
A (Å)	13.2840(10)	13.3109(12)	8.4252(9)	10.1342(10)	26.557(2)
<i>B</i> (Å)	16.1915(15)	14.5142(12)	24.270(3)	17.186(2)	7.0143(8)
C (Å)	13.6370(12)	17.405(6)	10.7163(12)	17.838(2)	26.686(2)
α (°)	90	101.217(3)	90	90	90
β(°)	98.972(4)	101.769(3)	101.483(3)	91.672(3)	118.652(3)
γ (°)	90.00	98.852(3)	90	90	90
V, Å	2897.3(4)	3162.7(5)	2147.4(4)	3105.5(5)	4362.3(7)
Ζ	4	2	4	4	8
Т (К)	100(2)	100(2)	100(2)	100(2)	100(2)
$ ho_{ m calc.}~(m g~cm^{-3})$	1.256	1.339	1.495	1.483	1.492
Reflections collected $(2\Theta_{max})$	65433/60.00	62261/62.00	34574/61.92	82019/62.00	125768/63.12
Unique reflections $(I > 2\sigma(I))$	8447/6851	20132/15830	6805/5278	9798/8658	14546/12335
Number of parameters (restraints)	222/1	815/31	288/0	398/6	559/0
λ (Å)/ μ (K α) (cm ⁻¹)	0.71073/7.57	0.71073/4.36	0.71073/10.10	0.71073/12.34	0.71073/13.34
$R_1^{\rm a}$ /goodness of fit ^b	0.0410/1.060	0.0489/1.020	0.0486/1.074	0.0841/1.194	0.0365/1.063
$wR_2^c (I > 2\sigma (I))$	0.0816	0.1074	0.0883	0.2363	0.0714
Residual density (e Å ⁻³)	+0.46/-0.26	+1.24/-1.14	+0.49/-0.45	+2.200/-0.784	+0.49/-0.36

Observation criterion: $I > 2\sigma(I)$. $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$.

 $\begin{aligned} & \text{GOF} = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}, \\ & wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2} \text{ where } w = 1/\sigma^2(F_o^2) + (aP)^2 + bP, P = (F_o^2 + 2F_c^2)/3. \end{aligned}$

lence region and contain a polarizing set of d functions on the non-hydrogen atoms [24]. Auxiliary basis sets used to expand the electron density in the calculations were chosen to match the orbital basis. The self-consistent field calculations were tightly converged $(1 \times 10^{-8} E_h \text{ in energy}, 1 \times 10^{-7} E_h \text{ in the den$ sity charge, and 1×10^{-7} in the maximum element of the DIIS [26] error vector). The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints. Electronic energies and properties were calculated using the B3LYP functional [27]. In this case, with the same basis sets as for the optimizations. Natural population analysis [28] was done through an interface of ORCA to the gennbo program version 5.0. Corresponding [29] and canonical orbitals and density plots were obtained using Molekel [30]. We describe our computational results for 3 using the broken-symmetry (BS) formalism [11,31].

3. Results and discussion

3.1. Synthesis and characterization

Two equivalents of the ligand 4,6-di-tert-butyl-2-[(2-pentafluorophenyl)-amino]benzenethiolate H₂(²L), prepared according to Ref. [11], were combined with one equivalent of CoCl₂ and four equivalents of triethylamine in acetonitrile under anaerobic conditions. A brief exposure to the atmosphere followed by addition of tetraphenylphosphonium bromide lead to the isolation of dark blue [PPh₄][Co^{III}(²L)₂] (**2**) in high yields. This compound is readily oxidized by iodine (Eq. (1)) to the neutral species $[Co^{III}(^{2}L)_{2}I]^{0}$ (3), which was isolated as black microcrystalline powder.

$$[PPh_4] \Big[Co^{III}(^2L)_2 \Big] + I_2 \rightarrow \Big[Co^{III}(^2L')_2 I \Big]^0 + [PPh_4]^+ + I^-$$
(1)

The oxidation of **2** to **3** is predominately ligand-based, as detailed below. Similar complexes of this type have been described recently [32].

Dark aubergine $[Co^{III}({}^{4}L)]^{0}$ (**4**) was simply prepared via a toluene reflux of the dark brown $[Co^{II}({}^{3}L)_{2}]^{0}$ precursor in a synthesis devised by Kawamoto et al. [13] depicted in Scheme 3. This method has been used to prepare analogous complexes with other metals [13,33]. The neutral compound $[Zn^{II}({}^{3}L)_{2}]^{0}$ (**6**) was prepared by the combination of zinc acetate and 2-phenylbenzothiazoline in methanol. In contrast to the cobalt compound, refluxing 6 in toluene did not result in any formation of [Zn^{II}(⁴L^{..})]⁰ [14].

3.1.1. Crystal structure determination

The crystal structures of complexes 1, 2, 4, 5, and 6 have been determined by single crystal X-ray crystallography at 100(2) K by using Mo Ka radiation. Fig. 1 displays the structures of the monoanions in 1 and 2. whereas the structures of the monoanion in 5 and neutral **6** are shown in Fig. 2. The structure of the neutral molecule in **4** is very similar to that on the monoanion in **5** and is shown in the Fig. S1. Selected bond distances and angles are presented in Tables 2 and 3.

Both monoanions in 1 and 2 are strikingly square planar with a trans-CoN₂S₂ moiety, where the cobalt ion occupies a crystallographic inversion center ($\alpha = 0.0^{\circ}$). For **2**, the bulky pentafluorophenyl substituents are parallel with respect to each other and make a dihedral angle of 79.1° to the CoN₂S₂ plane. The average C-S, C-N, and aromatic C-C distances are indicative of the presence of two identical o-iminobenzenethiolate(2-) ligands (type C, Scheme 2) rendering the oxidation state of the central cobalt ion +III. Thus the structural formulae [Co^{III}(abt)₂]¹⁻ and $[Co^{III}(^{2}L)_{2}]^{1-}$ represent the correct oxidation level of the ligands (type C, Scheme 2) and of the central cobalt ion.

The structures of the neutral complex in 4 and of the monoanion in 5 are also similar; both contain a nearly perfect square planar cis-CoN₂S₂ unit. The dihedral angle between the two CoNS planes, α , is 8.8° and 2.2° for **4** and **5**, respectively. The phenyl substituents of the alkane bridge are trans with respect to the CoN₂S₂ plane, making dihedral angles of 89.5° and 82.4°, and 89.3° and 84.4° for 4 and 5, respectively, and are also nearly parallel to each other (4: 11.4°; 5: 22.6°). In the monoanion the average C-S bond at 1.76(1)Å and the average C-N bond at 1.38(1) Å describe a closed-shell tetraanion $({}^{4}L)^{4-}$ (each aminobenzenethiolate arm type C, Scheme 2) which again renders the oxidation state of the central cobalt ion +III: $[Co^{III}(^{4}L)]^{1-}$. In the corresponding neutral complex, the C-S distance in shorter at 1.737 ± 0.006 Å as is the average C–N bond at 1.367 ± 0.01 Å. These distances are intermediate between those of a dianion



Fig. 1. Perspective views of the monoanions in crystals of 1 (top) and 2 (bottom).

type C and a π radical monoanion of type D (Scheme 2). Thus, the neutral form contains a one (delocalized) π radical ligand, $({}^{4}L{}^{})^{3-}$, and a Co(III) central ion: $[Co^{III}({}^{4}L{}^{})]^{0}$.

Finally, the neutral complex in **6** contains a tetrahedral ZnN₂S₂ polyhedron (α = 81.4°) with two *N*,*S*-coordinated, closed-shell monoanions (^{3}L)^{1–}. The average C–S distance is long at 1.76 Å and the average C–N double bond length is observed at 1.29 Å characteristic for type B ligands.

3.1.2. Electro- and spectroelectrochemistry

Cyclic voltammograms of complexes have been recorded at 25 °C in CH_2Cl_2 solutions containing 0.1 M $[N(n-Bu)_4]PF_6$ supporting electrolyte at a glassy carbon working electrode at scan rates of 25–800 mV s⁻¹. All potentials listed in Table 4 and referenced versus the ferrocenium/ferrocene couple (Fc⁺/Fc).

The CV of **1** recorded in the range of -0.2 to 2.0 V displays a reversible one-electron oxidation at $E_{1/2}^2 = -0.61$ V and a quasi-reversible reduction at $E_{1/2}^2 = -1.73$ V that are assigned as in Eq. (2). The one-electron electrochemical or chemical oxidation affords the neutral species that rapidly dimerizes to $[Co^{III}(abt)(abt)]_2$ [32,34]. The presence of the pentafluorophenyl substituents on $(^{2}L)^{2-}$, and phenyl groups on the bridge in $(^{4}L)^{4-}$, prevent similar processes occurring in **2** and **4**.

$$\left[Co^{II}(abt)_2 \right]_{\substack{S=1/2}}^{2-} \stackrel{-e}{\underset{+e}{\rightleftharpoons}} \left[Co^{III}(abt)_2 \right]_{\substack{S=1}}^{1-} \stackrel{-e}{\underset{+e}{\rightleftharpoons}} \left[Co^{III}(abt)(abt^{*}) \right]_{\substack{S=1/2}}^{0}$$
(2)

The CV of **2** recorded in the range -2.0 to 1.0 V is shown in Fig. S3. Three one-electron transfer waves have been observed: $E_{1/2}^2 = -1.54$ V; $E_{1/2}^2 = -0.37$ V; $E_{1/2}^2 = -7.1$ V that may be assigned to the processes described by Eq. (3).

$$\frac{[\operatorname{Coll}({}^{2}\mathrm{L})_{2}]^{2-}}{\overset{-e}{+e}} \xrightarrow{[\operatorname{Colll}({}^{2}\mathrm{L})_{2}]^{1-}} \xrightarrow{\stackrel{-e}{+e}}{\overset{+e}{+e}} \frac{[\operatorname{Colll}({}^{2}\mathrm{L})({}^{2}\mathrm{L}^{*})]^{0}}{\overset{+e}{||-e}} \xrightarrow{[\operatorname{Colll}({}^{2}\mathrm{L})]^{1+}}$$

$$\frac{[\operatorname{Colll}({}^{2}\mathrm{L})]^{1+}}{\overset{S=0}{\overset{=0}{\overset{=0}{\overset{-$$

The CV of **4** recorded in the range -2.0 to 0.5 V also displays three transfer waves (Fig. 3). The one-electron reduction and oxidation processes are fully reversible, whereas the second one-electron reduction to the dianionic species is only quasi-reversible as determined by controlled potential coulometry; the CV after coulometric reduction exhibiting new peaks. Despite the diminished intensity for the reversible oxidation, all three waves represent one-electron processes and the electron transfer series is summarized in Eq. (4).

$$\left[\operatorname{Co}^{\mathrm{II}}({}^{4}\mathrm{L}) \right]^{2-} \stackrel{-\mathrm{e}}{\underset{+\mathrm{e}}{\rightleftharpoons}} \left[\operatorname{Co}^{\mathrm{III}}({}^{4}\mathrm{L}) \right]^{1-} \stackrel{-\mathrm{e}}{\underset{+\mathrm{e}}{\rightleftharpoons}} \left[\operatorname{Co}^{\mathrm{III}}({}^{4}\mathrm{L}^{\cdot}) \right]^{0} \stackrel{-\mathrm{e}}{\underset{+\mathrm{e}}{\rightleftharpoons}} \left[\operatorname{Co}^{\mathrm{III}}({}^{4}\mathrm{L}^{\cdot}) \right]^{1+} (4)$$

The electronic spectra of **1**, **1**^{ox}, **2**, and **3** are overlaid in Fig. 4. Monoanionic 1, 2 and 5 possess a similar profile, that is, two intense bands ($\epsilon \approx 10^4 \, M^{-1} \, cm^{-1}$) in the far visible region between 500 and 700 nm (Table 5). The more prominent band at higher energy has been described as a $1b_{1u} \rightarrow 2b_{2g}$ transition composed of a mixture of ligand-to-ligand (LLCT) and ligand-to-metal (LMCT) charge transfer character owing to the considerable ligand content of the acceptor orbital (see DFT calculations) [6,9,32]. Importantly, no monoanionic species has any transitions in the near IR region that is a fingerprint for a ligand mixed valency giving rise to an intervalence charge transfer (IVCT) band. Similar spectra have been recorded for square planar monoanionic cobalt complexes with dithiolene, o-iminophenolate, and diimine ligands two [6,7,9,32,35–38]. In all cases, the absence of near IR bands supports an oxidation state of +III for the central cobalt ion.

The electronic spectrum of **4** has one very intense band at 658 nm ($\varepsilon = 3.9 \times 10^4 \, \text{M}^{-1} \, \text{cm}^{-1}$) and one moderately intense band at 805 nm (7800 M⁻¹ cm⁻¹) that are described as LMCT transitions (Fig. 5). Most importantly, there is a noticeable IVCT band at 1382 nm (3240 M⁻¹ cm⁻¹) that has been observed previously in the spectra of neutral cobalt complexes with similar ligands [6,7,35–38]. Treatment of **1** with one equivalent to ferrocenium hexafluorophosphate yielded [Co(abt)₂]⁰, whose electronic spectrum shown in Fig. 4, has a relatively weak band at 1173 nm (1500 M⁻¹ cm⁻¹). This IVCT band indicates ligand mixed valency in these neutral species whose electronic structure is defined as [Co^{III}(L)(L[·])].

Oxidation of 4 yields a species without any features in the near IR region (Fig. 5). This monocationic species is described as [Co^{III}(⁴L^{..})]¹⁺ where both arms of the tetradentate ligand have been one-electron oxidized to π radical oxidation level (type D). Its spectrum is similar in band position and intensity to the monoanionic complexes 1, 2, and 5, and that for five-coordinate 3, which has the formula [Co^{III}(²L')₂I]⁰ (Fig. 4). Most interestingly, the latter has a reasonably intense band at 1339 nm (6800 M⁻¹ cm⁻¹). When compared to the electronic spectra of the corresponding [Fe^{III}(²L')I] [11], the Co analog has its most prominent transition 130 nm lower in energy than the Fe complex due to the larger effective nuclear charge of the cobalt ion that stabilizes the d orbital manifold. However, the Fe compound only has a weak shoulder at 822 nm $(\sim 3000 \text{ M}^{-1} \text{ cm}^{-1})$, so a shift of $\sim 500 \text{ nm}$ is too large to be attributed to the effective nuclear charge of cobalt alone. The exact nature of this transition is not known at this time, and highlights the complexity of the intrinsic electronic structures of these compounds where two redox active ligands are bound to a central Co ion, in that the highly covalent orbitals give rise to low-energy LLCT and/or LMCT bands.



Fig. 2. Perspective views of the monoanion in crystals of **5** (top) and the neutral molecule in crystals of **6** (bottom).

Charge neutral **6** has been diagnosed as $[Zn^{II}({}^{3}L)_{2}]^{0}$ with two monoanionic closed-shell ligands. This tetrahedral complex exhibits one weak CT band at 447 nm (2000 M⁻¹ cm⁻¹, Fig. S4). The most reduced member of this electron transfer series, dianionic $[Co^{II}({}^{4}L)]^{2-}$, has no prominent LMCT or LLCT bands (Fig. 5), which is consistent with a low-spin Co(II) central ion and one tetraanionic ligand. The spectral features between 500 and 800 nm are remnants of the monoanionic compound that underscore the quasireversible nature of this redox process.

3.1.3. Magnetochemistry

The temperature dependence of the molar magnetic susceptibilities of solid samples of complexes have been measured in the temperature range 3–300 K by using a SQUID magnetometer at 1.0 T external magnetic field. The results are summarized in Table 6. Fig. 6 shows the temperature dependence of the magnetic moment of **1**. Above 50 K, the complex shows a temperature independent magnetic moment of 2.90 μ_B indicating the presence of two unpaired electrons per cobalt ion (*S* = 1 ground state). The decrease of μ_{eff} at <50 K has been successfully modeled by a large zero field splitting of the *S* = 1 ground state into M_s = 0 and

 $M_{\rm s} = \pm 1$ levels. The experimental data were simulated with $|D| = 47 \text{ cm}^{-1}$ and g = 2.15, consistent with the values reported for the square planar complexes $[\text{Co}(\text{tbbdt})_2]^{1-}$ (tbbdt = 3,5-ditert-butylbenzene-1,2-dithiolate) [9] and $[\text{Co}(\text{tdt})_2]^{1-}$ (tdt = toluene-3,4-dithiolate) [39]. The sign of *D* was determined from variable temperature variable field (VTVH) measurements shown in the inset of Fig. 6: $D = +41.2 \text{ cm}^{-1}$; g = 2.003. Very similar results have been obtained for the monoanionic complexes **2** and **5**. Again an S = 1 ground state has been established for both, with the data successfully modeled using $|D| = 29.0 \text{ cm}^{-1}$ and g = 2.32, for **2** (Fig. S5), and $D = +31.0 \text{ cm}^{-1}$, E/D = -0.385 and g = 2.10 [40], for **5** (Fig. S6).

3.1.4. EPR spectroscopy

X-band EPR spectra have been recorded on electrochemically oxidized **1** and **2**. These two S = 1/2 neutral species have very similar EPR parameters, namely a rhombic g-tensor with very little anisotropy and a modest ⁵⁹Co (I = 7/2, 100% natural abundance) magnetic hyperfine coupling. Fig. 7 shows the spectrum of **1**^{ox}; the spectrum of **2**^{ox} is found in Fig. S7. Table 7 summarized the spin Hamiltonian parameters obtained from simulations of the spectra.

In contrast, the EPR spectrum of **4** has a large anisotropy ($\Delta g = 0.686$), with the magnetic hyperfine equivalent to the electrochemically generated species described above (Fig. 8). Clearly a different parentage of the unpaired spin is seen in **4** compared to **1**^{ox} and **2**^{ox}. Other chemically isolated neutral species with two noninnocent bidentate ligands exhibit similar *g* anisotropy and hyperfine couplings (Table 7) that are typical of cobalt-based paramagnets irrespective of how the spin system is defined [6–8,35,37,41,42]. The EPR spectra of the latter closely resemble that reported for octahedral Co(III) (d⁶, S_{Co} = 0) complex coordinated by π radical ligands, such as [(tren)Co^{III}(tmbdt')]²⁺ (tren = tris(2-aminoehtyl)amine; tmbdt = 3,6-bis(triemthylsilyl)benzene-1,2-dithiolate) [43].

In order to rationalize the different spin Hamiltonian parameters, it has been proposed that electrochemically generated **1**^{ox} and **2**^{ox} attract two adventitious water molecules that stabilize a diamagnetic, low-spin Co(III) central ion that is ligated by a π radical monoanion (L[·])^{1–} ($S_L = ^1/_2$). This is the analogous electronic structure to [(tren)Co^{III}(tmbdt[·])]²⁺. As detailed below, DFT calculations support such a structure, though crucially only the *cis*-aquo complex gives the desired spin ground state; the *trans*-aquo species is calculated as having a metal-centered singly occupied molecular orbital.

3.2. DFT calculations

3.2.1. Calculated geometries

All complexes were geometry optimized using ORCA at the BP86 level of theory. For monoanionic **1** and **2**, the computed structures are in very good agreement with the experimental data (Table 8). The Co–N and Co–S bond lengths are overestimated maximally by 0.01 Å. The most revealing bonds are the C–N, C–S, and C–C distances of the aromatic ring. In each case, the long C–N (~1.39 Å) and C–S (~1.78 Å) bonds, and essentially equivalent C–C distances (avg. 1.41 Å) support the presence of two *o*-aminobenzenethiolate(2⁻) ligands (type C, Scheme 2) in **1** and **2**. The pentafluorophenyl substituents in **2** are similarly positioned orthogonal (87°) to the CoN₂S₂ as in the crystal structure.

In the absence of a crystal structure, we have geometry optimized the neutral species $[Co(abt)_2]^0 (\mathbf{1}^{ox})$. This square planar molecule exhibits similar Co–N and Co–S bond lengths to those in the monoanion **1**, however, there are noticeable differences in the intraligand C–N, C–S and aromatic C–C distances. Somewhat shorter C–N (1.369 Å) and C–S (1.753 Å) bond lengths and a slight inequivalence of the C–C bonds in the aromatic ring are consistent

Table 2

Selected bond distances (Å) and angles (deg) in 1, 2-Et₂O, and 6.

Complex 1 Co(1)-S(1) N(1)-C(2) C(2)-C(3)	2.1872(4) 1.371(2) 1.406(2)	Co(1)-N(1) C(1)-C(2) C(3)-C(4)	1.840(1) 1.413(2) 1.385(2)	S(1)-C(1) C(1)-C(6) C(4)-C(5)	1.753(2) 1.393(2) 1.392(3)
S(1) - C(0) S(1) - N(1)	87.46(5)	α	0.0		
Complex 2 Co(1)-S(1) C(2)-C(7) C(4)-C(5) C(7)-N(8) Co(2)-S(31) C(32)-C(37) C(34)-C(35) C(37)-N(38)	2.1739(4) 1.414(2) 1.401(2) 1.402(2) 2.1687(4) 1.418(2) 1.398(2) 1.399(2)	Co(1)-N(8) C(2)-C(3) C(5)-C(6) N(8)-C(9) Co(2)-N(38) C(32)-C(33) C(35)-C(36) N(38)-C(39)	1.869(1) 1.412(2) 1.389(2) 1.409(2) 1.867(1) 1.413(2) 1.397(2) 1.415(2)	S(1)-C(2) C(3)-C(4) C(6)-C(7) S(31)-C(32) C(33)-C(34) C(36)-C(37)	1.766(2) 1.401(2) 1.404(2) 1.762(2) 1.402(2) 1.399(2)
S(1)-Co(1)-N(8)	86.41(4)	S(31)-Co(2)-N(38)	86.71(4)	α	0.0
Complex 6 Zn(1)-S(1) Zn(1)-N(27) C(1)-C(2) C(4)-C(5) N(7)-C(8) C(21)-C(22) C(24)-C(25) N(27)-C(28)	2.2728(5) 2.113(1) 1.402(2) 1.389(2) 1.293(2) 1.403(2) 1.386(2) 1.291(2)	Zn(1)-N(7) S(1)-C(1) C(2)-C(3) C(5)-C(6) S(21)-C(21) C(22)-C(23) C(25)-C(26)	2.093(1) 1.762(2) 1.384(2) 1.400(2) 1.758(2) 1.381(2) 1.395(2)	Zn(1)-S(21) C(1)-C(6) C(3)-C(4) C(6)-N(7) C(21)-C(26) C(23)-C(24) C(26)-N(27)	2.2646(2) 1.407(2) 1.391(3) 1.429(2) 1.405(2) 1.386(3) 1.435(2)
S(1)-Zn(1)-N(7)	88.29(4)	S(21)-Zn(1)-N(27)	88.57(4)	α	81.4

Table 3

Selected bond distances (Å) and Angles (deg) in ${f 4}$ and ${f 5}$ -0.5 MeCN (in brackets).

Co(1)-S(1)	2.1384(6)	[2.173(3)]	N(7)-C(8)	1.470(3)	[1.469(14)]
Co(1)-S(12)	2.1388(6)	[2.168(3)]	C(8)-C(9)	1.556(3)	[1.399(15)]
Co(1)-N(7)	1.816(2)	[1.826(10)]	C(9)-N(10)	1.465(3)	[1.466(15)]
Co(1)-N(10)	1.815(2)	[1.825(10)]	N(10)-C(11)	1.371(3)	[1.380(14)]
S(1)-C(1)	1.738(2)	[1.760(12)]	C(11)-C(16)	1.411(3)	[1.404(17)]
C(1)-C(6)	1.417(3)	[1.425(16)]	C(16)-C(15)	1.390(3)	[1.398(18)]
C(1)-C(2)	1.398(3)	[1.399(15)]	C(15)-C(14)	1.395(3)	[1.38(2)]
C(2)-C(3)	1.379(3)	[1.393(18)]	C(14)-C(13)	1.377(3)	[1.39(2)]
C(3)-C(4)	1.407(3)	[1.400(18)]	C(13)-C(12)	1.397(3)	[1.389(17)]
C(4) - C(5)	1.372(3)	[1.391(17)]	C(12)-C(11)	1.413(3)	[1.407(18)]
C(5)-C(6)	1.411(3)	[1.410(16)]	C(12)-S(12)	1.735(2)	[1.765(13)]
C(6)-N(7)	1.365(3)	[1.367(14)]			
S(1)-Co(1)-N(7)	89.02(6)	[89.0(3)]	N(10)-Co(1)-S(12)	89.41(6)	[88.8(3)]
α	8.8	[2.2]			

Table 4

Redox potentials (V) of complexes versus Fc^+/Fc .

Complex ^a	$E_{1/2}^{1 b}$	$E_{1/2}^2^c$	$E_{1/2}^{3 d}$
1 2 4	–1.73 qr –1.54 r –1.81 gr	-0.61 r -0.37 r -0.61 r	+0.71 qr -0.04 r

r = Reversible; qr = Quasi-reversible.

 a Recorded in CH_2Cl_2 solutions containing 0.1 M [N(n-Bu)_4]PF_6 at 20 $^\circ C$ using a scan rate of 100 mV s $^{-1}$

^b 1–/2– Couple.

 $^{\rm c}$ 0/1 – Couple.

^d 1+/0 Couple.

with a Co(III) ion bound by one *o*-aminobenzenethiolate(2–) and one *o*-iminothiobenzosemiquinone(1–) π radical (Table 8). The optimized structure suggests the unpaired ligand spin is delocalized, though this may not be the case in the compound itself. In the interest of the measured EPR spectrum for this S = 1/2 species, we have added two water molecules to the system and generated a six-coordinate [Co^{III}(abt)(abt)(OH₂)₂]. This complex has been examined by theoretical calculations, where both the *cis*- and



Fig. 3. Cyclic voltammogram of **4** in a CH₂Cl₂ solution (0.10 M [N(*n*-Bu)₄]PF₆) at -5 °C with a scan rate of 100 mV s⁻¹ (glassy carbon working electrode). Potentials are references versus the *Fc*⁺/*Fc* couple.

trans- $[Co^{III}(abt)(abt)(OH_2)_2]$ forms have been geometry optimized. The *trans* isomer was a meager 2.6 kcal mol⁻¹ more stable than the *cis* conformation, however the latter had Co–OH₂ bonds at 2.116 Å



Fig. 4. Electronic spectra of 1 (black), 1^{ox} (red), 2 (green), and 3 (purple) in CH₂Cl₂ solutions at 20 °C.

Table 5					
Electronic s	pectra	of com	plexes ir	1 CH ₂ Cl ₂	solutions.

Complex	$\lambda_{\rm max} ({\rm nm}) (\epsilon, 10^4{ m M}^{-1}{ m cm}^{-1})$
1 ^{ox}	1173 (0.15), 799 (0.40), 656 (1.39)
1	695 (sh, 1.31), 664 (1.37), 566 (1.95), 512 (sh, 0.79), 385 (sh, 0.97)
2	743 (1.40), 617 (2.33), 552 (sh, 0.84), 365 (2.43)
3	1339 (0.68), 881 (1.18), 736 (2.77), 560 (sh, 0.51)
4 ¹⁺	756 (0.66), 592 (1.51), 500 (sh, 0.54), 346 (sh, 1.10)
4	1386 (0.32), 805 (0.78), 658 (3.91), 557 (sh, 0.50), 342 (sh, 1.01)
4 ^{1-a}	867 (0.14), 634 (0.61), 570 (1.59), 538 (sh, 0.57), 504 (0.42), 426
	(sh, 0.38), 354 (sh, 0.90)
4 ²⁻	413 (sh, 0.59), 344 (sh, 1.98)
6	447 (0.20)

^a Complex 5.

and 2.154 Å similar to reported cobalt-aquo compounds [44], whereas the *trans* structure was discounted by the very long bonds at 2.43 Å. Both the Co–L and intraligand distances are similar to the four-coordinate species and suggest a Co(III) ion with one coordinated ligand radical. The O–Co–O angle is at 79.5° while the two CoNS planes meet with a dihedral angle of 84.6°.

The geometry optimized structure of $[Co^{III}(^{2}L')_{2}I]^{0}$ (**3**) exhibits even shorter C–N and C–S bond lengths than observed in **1**^{ox}. Furthermore, there is a pronounced quinoidal distortion of the aromatic ring. This distances are reminiscent of the intraligand bond lengths in crystallographically characterized $[Pt^{II}(^{2}L')_{2}]^{0}$ and geometry optimized iron analogue $[Fe^{III}(^{2}L')_{2}I]^{0}$ [11], such that we can described this five-coordinate complex as a Co(III) ion bound by one apical iodo at 2.468 Å that is typical of similar complexes [6,32], and two *o*-iminothiobenzosemiquinone(1–) π radial ligands.

The geometry optimized structures of neutral **4** and monoanionic **5** have intraligand bond distances in reasonable agreement with their crystal structures. The slight shortening of the C–N and C–S bond lengths in **4** a consequence of some ligand radical character, similar to that calculated for 1^{ox} and 1^{ox} ·2H₂O. Moreover, the pendant phenyl groups are nearly orthogonal to the CoN₂S₂ plane in each case (~87°) and the small twist of the geometry about the Co ion toward a tetrahedron is mapped at 5.0° and 4.2° for **4** and **5**, respectively, and in excellent agreement with the crystallographic data.



Fig. 5. Electronic spectra of $[4]^{1+}$ (purple), [4] (black), $[4]^{1-}$ (red), and $[4]^{2-}$ (blue) in CH₂Cl₂ solution (0.10 M [N(*n*-Bu)₄]PF₆) at -5 °C.

3.2.2. Bonding schemes

The bonding schemes in monoanionic and neutral $[Co(L)_2]^{1-}$ have been examined previously using both ab initio and DFT methods. The outcome of these studies, with either two α -diimine [6,36], α -iminopyridine [37,38], o-aminophenolate [6,41], or dithiolene ligands [9,35], was that a complicated electronic structure arose since the energy of the cobalt d orbitals is comparable to the energy of the ligand π orbitals. Despite these systems containing two asymmetric aminobenzenethiolate ligands, they possess approximate D_{2h} point symmetry due to their square planarbased geometries.

The calculated electronic ground state is ${}^{3}B_{1g}$ with the following electronic configuration: $(1a_g)^2(2a_g)^2(1b_{3g})^2(1a_u)^2(1b_{2g})^2(1b_u)^2$ $(2b_{2g})^{1}(2b_{3g})^{1}(1b_{1g})^{0}$ (Fig. 9). However, despite the MO manifold showing two doubly occupied d orbitals, two singly occupied d orbitals and one empty d_{xy} orbital that is considered the hallmark for an intermediate-spin Co(III) ion, assigning an unambiguous spectroscopic oxidation state for the metal (and oxidation level to the ligands) is rendered impossible due to the considerable ligand character in the 2b_{2g} orbital (Table 9). The actual electronic structure of monoanionic complexes at this time is best reprethe following resonance forms $[Co^{III}(L^{2-})]$ sented by $(L^{2-})^{1-} \leftrightarrow [Co^{II}(L^{2-})(L^{1-})]^{1-} \leftrightarrow [Co^{II}(L^{1-})(L^{2-})]^{1-}$. The Mulliken spin population analysis finds 1.61 α -spins (spin-up) at the cobalt ion that indicates a slightly greater weight to the Co(III) form (Fig. 10; Table 10), and we have written the formula as such throughout this article.

It has been argued that the description of neutral $[Co(L)_2]^0$ in terms of a single configuration is slightly oversimplified, but for all practical purposes adequate [6]. One-electron oxidation of monoanion 1 occurs with the removal of an electron from the singly occupied $2b_{2g}$ orbital such that it is now the LUMO of $[Co(^{2}L)_{2}]^{0}$ (Fig. 9). The highest occupied orbital is the Co-based 2b_{3g} SOMO, such that the calculated electronic configuration for this $S = \frac{1}{2}$ species is then $(1a_g)^2(2a_g)^2(1b_{3g})^2(1a_u)^2(1b_{2g})^2(1b_u)^2(2b_{3g})^1(2b_{2g})^0$ $(1b_{1g})^0$. Unlike that observed for the analogous bis(diimine) complexes [6], the oxidation does not result in any substantial changes to the compositions of the $2b_{2g}$ and $2b_{3g}$ orbitals, however there is a marked increase in the Co d_{xz} character in the $1b_{1g}$ orbital (from 32.5% in 1 to 62.3% in 1°x, shown in blue in Fig. 9). Again, like the monoanionic species, the pervasive covalency in this neutral species renders a physical oxidation assignment of the metal impossible, such that we can only represent the electronic structure by the

Table 6

Magnetochemical data of complexes 1, 2, 4, and 5.

Complex	S ^a	$\mu_{ m eff}$	$D^{\mathbf{b}}$	g
1 2 ^c 4 5 [N(<i>n</i> -Bu) ₄][Co ^{III} (bdt) ₂] ^d	1 1 1/2 1 1	$\begin{array}{c} 2.90 \\ 3.22 \\ \mu_{B} \\ 80-300 \\ K \\ 1.93 \\ \mu_{B} \\ (20-300 \\ K \\ 3.00 \\ \mu_{B} \\ (50-300 \\ K \\ \end{array}$	+41.2 +29.0 +31.0 +37.4	2.003 2.32 2.28 2.10 2.19
$\begin{split} & [N(n-Bu)_4][Co^{III}(tdt)_2]^{\alpha} \\ & [N(n-Bu)_4][Co^{III}(tbbdt)_2]^{e} \\ & [N(n-Bu)_4][Co^{III}(tmbdt)_2]^{f} \\ & [CoCp_2][Co^{III}(L_{N,O})_2]^{g} \end{split}$	1 1 1 1	2.80 μ _B (50–300 K) 2.84 μ _B (50–300 K) 3.10 μ _B (50–300 K)	+39.4 +32.0 +35.0 +57.0	2.09 2.17 2.094 2.26

^a Total spin ground state.

^b In cm⁻¹. The sign of *D* was determined by VTVH magnetization measurements at 1.0, 4.0, 7.0 T.

^c No VTVH data obtained, however, *D* is assumed to be positive.

^d $(bdt)^{2-}$ = Benzene-1,2-dithiolate. Ref. [39].

Ref. [9].

^f (tmbdt)²⁻ = 3,6-Bis(trimethylsilyl)benzene-1,2-dithiolate. Ref. [35].

^g $(L_{N,O})^{2-} = 2-(2-Trifluoromethyl)aniline-4,6-di-$ *tert*-butylphenol. Ref. [6].



Fig. 6. Temperature-dependence of the magnetic moment, μ_{eff} , μ_{B} , of a powdered sample of 1 recorded in a 1.0 T external magnetic field. The filled squares represent the experimental data, whereas the solid line represents the simulation (g = 2.153; $|D| = 47.1 \text{ cm}^{-1}$; TIP = $-417 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$). Inset shows the variable field and variable temperature dependence of the magnetization of 1. The solid lines represent best fits obtained using g = 2.003, D = +41.2 cm⁻¹, and S = 1.



Fig. 7. X-band EPR spectra of 1^{ox} at 10 K in CH₂Cl₂ solution containing 0.1 M [N(n-Bu)₄]PF₆ (conditions: frequency 9.63 GHz; power 0.1 mW; modulation 0.75 mT). Experiment (solid line) and simulation (dashed line).

following resonance structures: $[Co^{III}(L^{2-})(L^{1-})]^0 \leftrightarrow [Co^{III}(L^{1-})]^0$ $(L^{2-})]^{0} \leftrightarrow [Co^{II}(L^{1-})(L^{1-})]^{1-}$. The spin density plot of **1**^{ox} exhibits 1.48 α -spins (spin-up) on Co and 0.3 β -spins (spin-down) on the ligands that lends more weight to the Co(III) structure (Fig. 10). Throughout this manuscript we documented such an oxidation state in the formulae for these neutral species. A similar distribution is found in the spin density plot of 4 (Fig. S9), where in concert with the crystallographic parameters, a Co(III) central ion is favored.

As shown in the electron configuration of **1**^{ox}, the unpaired electron located in the d_{yz} orbital should lead to a significantly large g anisotropy that is clearly not evident in the EPR spectrum of this coulometrically generated neutral species. Interestingly, the EPR spectrum of **4** is highly anisotropic, such that while it is also ex-

Table 7				
EPR Spin Hamiltonian g-tensor and	59 Co magnetic hyperfine tensor (A \times 10 ⁻⁴	⁴ cm ⁻¹) derived fro	om simulation of frozen s	olution spectra.

Complex	g _x	g_y	gz	<g>^a</g>	Δg^{b}	A _{xx}	A _{yy}	Azz	<a>^c	Reference
1 ^{ox}	2.004	2.004	2.008	2.005	0.004	43	0	16	19.7	This work
2 ^{ox}	2.046	2.030	2.028	2.035	0.018	19	0	69	29.3	This work
4	2.016	2.046	2.702	2.255	0.686	18	0	28.4	15.5	This work
[Co ^{III} (tren)(tmbdt)] ²⁺	2.000	2.018	2.036	2.018	0.036	4.7	30	4.7	13.1	[43]
[Co ^{III} (tmbdt)(tmbdt ⁻)(OH ₂) _x] ⁰	2.005	2.032	2.050	2.029	0.045	-1.3	54.5	7.3	20.2	[35]
$[Co^{II}(L_{0,0})_2(Et_2O)]^{0 d}$	2.32	2.81	3.45	2.86	1.13	17	34	190	80.3	[42]
$[Co^{II}(L_{0,0})_2]^{2-e}$	1.97	2.30	2.71	2.327	0.74	37	80	49	55.3	[42]
$[Co(L_{N,N})_2]^{0 f}$	1.991	2.051	2.810	2.284	0.819	25.6	0	44.8	23.5	[6]
$[Co(L_{Npy})_2]^{0 g}$	2.05	1.91	3.53	2.497	1.48	25	30	140	65	[37]
$[Co(L_{N,O})_2]^{0 h}$	1.949	1.936	3.620	2.502	1.671	50	52.2	240	114.1	[41]

 $\langle g \rangle = (g_x + g_y + g_z)/3.$

 $\Delta g = g_z - g_x$.

 $<A> = (A_{xx} + A_{yy} + A_{zz})/3.$

 $(L_{0,0};)^{1-}$ = bis(2,6-isopropylphenyl)glyoxyl π radical.

 $(L_{0,0})^{2-}$ = bis(2,6-isopropylphenyl)glyoxylate.

^f $L_{N,N} = N$ -phenyl-o-phenylenediimine.

 $L_{Npy} = \alpha$ -Iminopyridine.

^h $L_{N,O} = \alpha$ -Iminoketone.



Fig. 8. X-band EPR spectra of **4** in a CH_2Cl_2 /toluene solution at 10 K (conditions: frequency 9.44 GHz; power 0.1 mW; modulation 1.0 mT). Experiment (solid line) and simulation (dashed line).

plained by the aforementioned resonance forms, we can furthermore add that the total doublet ground state results from either a high-spin Co(II) $S_{Co} = {}^{3}/_{2}$ central ion antiferromagnetically coupled to two ligand π radical monoanions ($S_{L} = 1$), or an intermediate-spin Co(III) $S_{Co} = 1$ antiferromagnetically coupled to one ligand π radical monoanion ($S_{L} = {}^{1}/_{2}$). The net result in both instances is a metal-centered doublet ground state.

The stark difference in the *g* anisotropy between 1^{ox} and 2^{ox} on the one hand, and **4** on the other has been ascribed to inclusion of two adventitious water molecules in the former to give a six-coordinate species [Co^{III}(L)(L')(OH₂)₂]. Only the *cis* conformation yielded the correct electronic structure, that as an octahedral

Table 8

Calculated and experimental (in parentheses) bond lengths (Å) in 1, 2, 1^{ox}, 1^{ox}, 2H₂O, 3, 4, and 5.



	1	2	1 ^{ox}	1°x.2H20		3	4	5
Co-N	1.846 (1.840)	1.880 (1.869)	1.819	1.888	1.842	1.878	1.821 (1.816)	1.838 (1.826)
Co-S	2.196 (2.187)	2.183 (2.179)	2.174	2.176	2.261	2.176	2.154 (2.139)	2.187 (2.171)
C-N	1.378 (1.371)	1.403 (1.402)	1.369	1.361	1.375	1.374	1.377 (1.368)	1.385 (1.374)
C–S	1.781 (1.753)	1.784 (1.766)	1.753	1.766	1.763	1.728	1.757 (1.737)	1.785 (1.763)
C1-C2	1.431 (1.413)	1.428 (1.414)	1.434	1.442	1.436	1.441	1.436 (1.414)	1.433 (1.415)
C1-C6	1.421 (1.393)	1.413 (1.404)	1.422	1.428	1.424	1.426	1.423 (1.401)	1.421 (1.404)
C2-C3	1.405 (1.406)	1.424 (1.412)	1.410	1.411	1.411	1.441	1.410 (1.406)	1.404 (1.403)
C3-C4	1.411 (1.385)	1.419 (1.401)	1.401	1.404	1.404	1.397	1.400 (1.388)	1.411 (1.391)
C4-C5	1.410 (1.392)	1.410 (1.401)	1.418	1.419	1.416	1.433	1.416 (1.392)	1.408 (1.395)
C5-C6	1.406 (1.390)	1.408 (1.389)	1.396	1.396	1.398	1.388	1.397 (1.384)	1.407 (1.386)

geometry that stabilizes a low-spin Co(III) ion with one unpaired electron residing in a predominantly (87%) ligand-centered orbital (Scheme S2). Three doubly occupied and two empty Co d orbitals describe a low-spin Co(III) $S_{Co} = 0$ central ion. This arrangement is directly analogous to $[(tren)Co^{III}(tmbdt)]^{2+}$ that possesses similar spin Hamiltonian parameters (Table 7) [43]. Interestingly, the *trans* structure gave rise to an intermediate-spin Co(III) $S_{Co} = 1$ antiferromagnetically coupled to one ligand π radical ($S_L = 1/2$). This resulted in a metal-centered d_{z^2} (2ag orbital) paramagnet which although consistent with the low g anisotropy of the EPR spectrum, a considerable Co 4s contribution would be expected to generate a sizeable magnetic hyperfine interaction.

The electronic structure of **3** was derived from a B3LYP BS(2,2) $M_{\rm S}$ = 1 single point calculation on the BP86 optimized coordinates. The MO manifold shown in Fig. 11 presents a d orbital occupancy consistent with an intermediate-spin $Co(III) S_{Co} = 1$. The binding of the iodo ligand lifts the Co ion out of the N_2S_2 plane, reducing the ligand character in the 2b_{2g} orbital that is now effectively a Cobased SOMO (78% metal character). The composition of the $2b_{3g}$ and 1b1g orbitals are the same for the monoanionic and neutral species described above. The two ligand-based SOMOs (79% and 80% ligand character, respectively) found in the spin-down manifold are antiferromagnetically coupled to the $S_{CO} = 1$ center that gives a $S_t = 0$ spin ground state. The orbital overlap integrals of S = 0.37 and S = 0.70 underscore the strength of the coupling in this system, similar to iron analogue [11]. Fig. 10 shows a spin density plot (Mulliken analysis) with α -spin density in red and β -spin density in yellow for 3.

4. Conclusions

Complexes of cobalt containing two bidentate or one tetradentate aminobenzenethiolate-based ligand have been prepared and their electronic structures characterized by spectroscopic and theoretical techniques. The consequence of the energetic equivalence of the Co 3d manifold and the ligand π orbitals delivers considerable ligand character to the frontier orbitals that precludes a definitive a physical oxidation state assignment to both the cobalt ion and the ligands. This is not a new concept, since several studies of various cobalt systems with different nitrogen-, oxygen-, and sulfur-donor noninnocent ligands have arrived at the same conclusion [6,9,42]. A comparison of the electron and spin distribution from a natural population analysis of various monoanionic cobalt



Fig. 9. Qualitative MO schemes for $[Co(abt)_2]^{1-}(1)$ and $[Co(abt)_2]^0(1^{0x})$. Kohn–Sham canonical orbitals are depicted for 1 (left) and 1^{0x} (right).

species (Table 11) shows a d population between 7.57 and 7.82 and the spin density ranging 1.47-1.78. The charge excess over the formal d⁶ or d⁷ electron configuration arises from the covalent population of the otherwise unpopulated Co d_{xy} orbital due to σ donation from the ligand. These values show the central ion to be more reduced than typical Co(III) and more oxidized than typical Co(II) complexes. Thus, in $[Co(L)_2]^{1-}$ the cobalt ion is somewhere between $Co(II) d^7$ and $Co(III) d^6$, and the electronic structure can only be represented by the resonance forms $[Co^{II}(L^{2-})(L^{2-})]^{1-} \leftrightarrow [Co^{II}(L^{2-})(L^{1-})]^{1-} \leftrightarrow [Co^{II}(L^{1-})(L^{2-})]^{1-}$. Despite the crystallographic analysis strongly favoring a Co(III) ion with two closed-shell ligands, there are several spectroscopic indicators for some partial Co(II)-ligand radical character in related systems [6,7,9,35,42,45]. A notable departure from this ambiguity is packaged in the form $[Co^{II}(L_{Npy})(L_{Npy})]^{1-}$ $(L_{Npy} = \alpha$ -iminopyridine) [38], with its diamagnetic ground state derived from antiferromagnetic coupling between a low-spin Co(II) ($S_{co} = 1/2$) and ligand π radical $(S_{\rm L} = 1/2)$.

For the neutral compounds, a similar degree of covalency is apparent, however there are contrasting spin state systems that give rise to the doublet ground state that are dependent on the noninnocent bidentate ligand involved. For $[Co^{II}(L_{O,O})_2(OEt_2)]^0$ [42], the spectroscopic, crystallographic and computational studies clearly indicate an electronic structure with a high-spin Co(II) ion $(S_{Co} = ^3/_2)$ antiferromagnetically coupled to two diketyl radicals $(S_L = 1)$. For square planar (or tetrahedrally distorted) bis(α -dii-

mines) complexes [6], the same electronic structure is not so apparent, however, the charge and spin population analysis favor a [Co^{II}(L_{N,N}')₂] with a *low-spin* Co(II) ($S_{Co} = 1/2$) antiferromagnetically coupled to one of two ligand π radicals ($S_L = 1$). The square planar [Co^{II}(L_{N,O}')₂]⁰ with two aminophenolate ligands has similar metric and spectroscopic parameters [6]. The tetrahedral analogues have been diagnosed as having a quartet ground state (S = 3/2) that arises from either: a) antiferromagnetic coupling between a high-spin Co(III) ion ($S_{Co} = 2$) and one ligand π radical

Table 9

Percentage composition of the selected orbitals of complexes as obtained from DFT (COSMO) calculation at the scalar relativistic ZORA-B3LYP Level with $\rm CH_2Cl_2$ as the solvent.

Complex	MO	$Co(d_{yz})$	$Co(d_{yz})$	$N(2p_z)$	$S(3p_z)$	$C(2p_z)^a$
1	2b _{3g}	79.9	57.0	1.2	5.2	6.2
	$2b_{2g}$			14.6	9.2	3.4
2	$2b_{3g}$	73.3	66.1	8.2	0.2	6.6
	$2b_{2g}$			5.0	16.2	1.2
1 ^{ox}	$2b_{3g}$	77.1	53.2	3.6	2.4	7.2
	$2b_{2g}$			12.8	17.2	3.4
4	$2b_{3g}$	75.0	50.1	3.4	3.1	4.7
	$2b_{2g}$			13.6	16.3	2.5
5	$2b_{3g}$	74.1	57.6	3.8	2.5	4.9
	$2b_{2g}$			12.0	11.3	1.4

^a The aromatic carbons bonded to the heteroatoms N and S.



Fig. 10. Mulliken Spin Density plots for (a) $[Co^{III}(abt)(abt)]^{1-}$ (1), (b) $[Co^{III}(abt)(abt)]^{0}$ (1^{ox}), (c) $[Co^{III}(abt)(abt)(OH_2)_2]^{0}$ (1^{ox}-2H₂O), and (d) $[Co^{III}(2L_2)_2]^{0}$ (3).

 Table 10

 Mulliken spin populations analyses as obtained from DFT (COSMO) calculation at the scalar relativistic ZORA-B3LYP level with CH₂Cl₂ as the solvent.

Complex	$ ho_{Co}$	$ ho_{ extsf{L}}^{ extsf{a}}$
1	+1.61	+0.39
2	+1.66	+0.34
1 ^{ox}	+1.48	-0.48
1 ^{ox} ·2H ₂ O	+0.06	+0.94
3	+1.55	-1.48
4	+1.44	-0.44
5	+1.58	+0.42

^a Spin density distributed on the aminobenzenethiolate ligands only.

monoanion ($S_L = 1/2$); or b) a high-spin Co(II) ion ($S_{Co} = 3/2$) bound by two closed-shell ligands [36]. This is contrasted here by $[Co^{III}(L_{N,S})(L_{N,S})]^0$, where a central cobalt ion in the +III oxidation state is the preferred structure, though reality from the perspective of a population analysis is again between a Co(II) and Co(III) resonance forms (Table 11). It can be seen that the aminobenzenethiolate ligand is more difficult to oxidized that its α -diimine, α -iminopyridine, diketonate, and aminophenolate analogues. This trend is realized through the diverse electronic structures arising from the various neutral compounds compared with their corresponding monoanionic species.

The electronic structure description for the five-coordinate $[Co^{III}(L)_2I]^0$, with either two aminophenolate or aminobenzenethiolate ligands, is more definitive, with both the spectroscopic and theoretical data supporting a intermediate-spin Co(III) central ion ($S_{Co} = 1$) antiferromagnetically coupled to two ligand π radicals ($S_L = 1$).

Among four-coordinate complexes of the first row transition metals with two noninnocent bidentate ligands, it is apparent that those with a cobalt central ion are the most perplexing. Cobalt occupies a unique position in the periodic table where the comparable energies of the Co 3d and ligand orbitals generate highly



Fig. 11. Qualitative MO scheme for neutral **3** (S = 0) as derived from a BS(2,2) DFT calculation (B3LYP/ZORA).

covalent systems that defy physical oxidation level (state) assignment to either the cobalt or the ligand.

Table 11

Comparison of the charge and spin populations at the Co ion resulting from a natural population analysis of the one-electron density of the ground state resulting from scalar relativistic ZORA-B3LYP DFT calculations in CH₂Cl₂ solution by using COSMO model

Complex	Electrons-3d	Electrons-4s	Spin-d	Reference
1	7.57	0.29	1.58	This work
1 ^{ox}	7.61	0.30	1.43	This work
$[Co^{III}(pda)_2]^{1-a}$	7.60	0.53	1.47	[6]
[Co ^{ll} (pda) ₂] ^{0 a}	7.64	0.51	1.14	[6]
$[Co^{III}(bdt)_2]^{1-b}$	7.82	0.51	1.59	[9]
[Co ^{III} (tmbdt) ₂] ^{1- c}	7.58	0.47	1.78	[35]

pda = *O*-phenylenediamine. b

bdt = Benzene-1,2-dithiolate.

^c tmbdt = 3,6-Bis(trimethylsilyl)benzene-1,2-dithiolate.

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Appendix A. Supplementary material

CCDC 720621, 720622, 720623, 720624 and 757525 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.03.042.

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