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# Electrochemical studies of cobalt(II) diphenylazodioxide complexes

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## ABSTRACT

The electrochemical behavior of the unusual cobalt(II) diphenylazodioxide complex salts  $[\text{Co}(\text{az})_4](\text{PF}_6)_2$  **1** and  $[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$  **2** has been studied by cyclic voltammetry. Each complex displays two quasireversible redox couples, which are proposed to correspond to a reduction of Co(II) to Co(I), followed by a ligand-based reduction. Irreversible reductions of **1** are observed at more negative potentials, and are proposed to arise from deposition of elemental Co and the decomposition of transiently formed Co(-I) species. Spectroelectrochemical experiments on both **1** and **2**, involving electrolytic reduction followed by reoxidation, are consistent with the quasireversibility observed in the CV measurements.

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## 1. Introduction

The concept of ligand-based redox activity is an important one in transition metal coordination chemistry. A redox-active or “non-innocent” ligand is one with more than one plausible charge for the purpose of defining the oxidation state of its associated metal. In a complex, these different assignments of charge are associated with electron transfer between the ligand and metal. The presence of redox-active ligands can thus make the assignment of metal oxidation state and ligand charge somewhat challenging, and the most accurate assignment of these values may depend strongly on the identity of the metal and its other ligands [1–3].

Perhaps the best-known redox-active ligand is the chelating diimine 2,2'-bipyridyl (bpy). For instance, the Ru(II) complex  $\text{Ru}(\text{bpy})_3^{2+}$  undergoes photoinduced metal-to-ligand charge transfer (MLCT) in which an electron is promoted from a predominantly Ru 4d-type molecular orbital (MO) to a primarily bpy  $\pi^*$  MO, leading to an electronic excited state in which the Ru center is Ru(III) [4–6]. Because of this excitation,  $\text{Ru}(\text{bpy})_3^{2+}$  can serve as a photosensitizer, as its excited state can mediate other chemical reactions. For example, Ru complexes with ligands derived from bpy have been used in water oxidation systems [7–10], and Yoon and coworkers have used salts of  $\text{Ru}(\text{bpy})_3^{2+}$  and related cations as photocatalysts for organic reactions such as [2 + 2] cycloadditions [11–13].

While Ru complexes with redox-active ligands have been extensively studied, the properties of cobalt complexes of bpy, 2,2':6',2''-

terpyridine (tpy), 1,10-phenanthroline (phen), and their derivatives have also been explored, particularly by electrochemical methods. Conradie and coworkers studied the electrochemical behavior of Co(II) polypyridine complexes such as  $\text{Co}(\text{bpy})_3^{2+}$ ,  $\text{Co}(\text{tpy})_2^{2+}$ , and analogous complexes with substituted bpy and tpy ligands. Cyclic voltammetry (CV) of these complexes in dry acetonitrile with 0.1 M  $^n\text{Bu}_4\text{NPF}_6$  supporting electrolyte showed three reversible redox couples for each ligand type: Co(III)/Co(II), Co(II)/Co(I), and Co(I)/Co(I)(L<sup>-</sup>), where the first two couples were assigned as Co-based redox processes, and the third was assigned to the one-electron reduction of a Co(I) complex to a Co(I) complex bearing a radical anion bpy or tpy ligand [14]. Notably, these studies found that the Co-based reductions of bpy complexes occurred at less negative reduction potentials when the bpy ligands contained less electron-donating substituents, indicating substantial involvement of the ligands even in reductions that are primarily Co-centered. The same authors observed an analogous set of reversible redox couples in electrochemical studies of  $\text{Co}(\text{phen})_3^{2+}$  and several similar complexes with substituted phen ligands. The reduction of the Co(II) complex of 5-nitro-1,10-phenanthroline, however, was found to be irreversible, and density functional theory calculations indicated that this reduction was ligand-centered [15]. Fontecave and coworkers prepared a series of eight  $\text{Co}(\text{tpy})_2^{2+}$  complexes with variously substituted tpy ligands and obtained CV data in acetonitrile with 0.1 M  $\text{LiNTf}_2$  ( $\text{Tf} = \text{SO}_2\text{CF}_3$ ). They found that the first redox couple, assigned as  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  based on DFT calculations was reversible for all eight complexes, while the second redox couple, at more negative potentials,

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Fig. 1. Cobalt(II) diphenylazodioxide complexes.

was either reversible or irreversible depending on the substituted tpy ligand. This second redox couple was assigned as Co(I)/Co(I)(L<sup>-</sup>) by DFT for each complex studied [16].

Cabral, MacFarlane, and coworkers studied the electrochemical behavior of Co(bpy)<sub>3</sub><sup>2+</sup> in the molecular solvents acetonitrile, methoxypropionitrile, and propylene carbonate, each containing 0.1 M <sup>n</sup>Bu<sub>4</sub>BF<sub>4</sub> as supporting electrolyte, as well as in four different ionic liquids: the B(CN)<sub>4</sub><sup>-</sup> and PF<sub>3</sub>(CF<sub>2</sub>CF<sub>3</sub>)<sub>3</sub><sup>-</sup> salts of the 1-ethyl-3-methylimidazolium cation, and the B(CN)<sub>4</sub><sup>-</sup> and NTf<sub>2</sub><sup>-</sup> salts of the 1-butyl-1-methylpyrrolidinium cation [17]. Unlike Conradie and coworkers [14], these authors found that, while the Co(III)/Co(II) couple was reversible, the Co(II)/Co(I) couple was chemically irreversible, which they proposed was due to dissociation of bpy from transient Co(bpy)<sub>3</sub><sup>+</sup>. In support of this hypothesis, the Co(II)/Co(I) couple was shown to be reversible in the presence of excess bpy in all solvents examined other than methoxypropionitrile [17].

Cobalt complexes with redox-active nitrogen ligands have been used in catalytic and biological applications. Kang and coworkers demonstrated that a Co(II) complex of an imino-substituted bipyridyl ligand was an efficient electrocatalyst for the electrochemical reduction of carbon dioxide to formate ion in acetonitrile [18], and Geneste and coworkers showed that Co(N-N)<sub>2</sub><sup>2+</sup>, where N-N = 4,4'-bis(hydroxymethyl)-2,2'-bipyridyl, catalyzed the reductive dichlorination of several chloroacetanilide pesticides of environmental concern in aqueous solution [19]. Alberto, Probst, and coworkers examined a series of Co(II) polypyridine complexes, and showed that they displayed photocatalytic activity for hydrogen generation from water [20]. The ability of Co(III) complexes of bpy or phen ligands to bind DNA was studied by Selvi and Palaniandavar [21] and by Athappan and coworkers [22].

In addition to ligands such as bpy, phen, and their derivatives, which are redox-active under photolytic or electrochemical conditions, some ligands undergo temperature-dependent exchange of electrons with their metal center. Pierpont and coworkers have studied the interactions of the dianionic 3,5-di-*tert*-butylcatecholato (DBCat<sup>2-</sup>) and monoanionic 3,5-di-*tert*-butylseminoquinone (DBSQ<sup>-</sup>) ligands with cobalt, and characterized the complex Co(bpy)(DBCat)(DBSQ), whose structural parameters, as established by single-crystal X-ray diffraction, indicated that this was, in the solid state, a Co(III) complex with one DBCat<sup>2-</sup> and one DBSQ<sup>-</sup> ligand. Magnetic data were consistent with this assignment [23]. Solution-phase spectroscopic analysis, however, suggested an equilibrium between Co(bpy)(DBCat)(DBSQ) and its electroisomer (a.k.a. valence tautomer), the Co(II) species Co(bpy)(DBSQ)<sub>2</sub>. This electroisomerization equilibrium is the result of an intramolecular electron transfer from the DBCat<sup>2-</sup> ligand to the Co(III) center, and its Co(II) product may be thought of as an unusually low-lying, thermally accessible electronic excited state [23]. By measuring the temperature dependence of the electroisomerization equilibrium constant, the thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  for the electroisomerization were obtained [24].

A comparatively little-known class of ligands are the *cis*-*N,N'*-azodioxides R(O)NN(O)R (R = alkyl or aryl), the dimers of nitrosoalkanes

or nitrosoarenes. Despite the ability of such ligands to bind to a metal center with both oxygen atoms, forming a five-membered chelate ring, only five azodioxide complexes have thus far been structurally characterized by single-crystal X-ray diffraction [25]. Hanusa and coworkers prepared the only main-group example thus far, the Ca(II) complex salt [Ca{Ph(O)NN(O)Ph}(H<sub>2</sub>O)<sub>2</sub>(THF)<sub>3</sub>]<sub>2</sub>I<sub>2</sub> [26], and Whiting and coworkers prepared the Sc(III), *d*<sup>0</sup> complex Sc{Ar(O)NN(O)Ar}(H<sub>2</sub>O)(OTf)<sub>3</sub> (Ar = 2-methoxyphenyl, Tf = SO<sub>2</sub>CF<sub>3</sub>) [27]. The first transition metal azodioxide complex with a partially filled *d* subshell was the Fe(II), *d*<sup>6</sup> azodioxide complex cation salt of an Fe(III) complex anion [Fe{Ph(O)NN(O)Ph}<sub>3</sub>](FeCl<sub>4</sub>)<sub>2</sub>, with trigonal prismatic geometry about the Fe center of the cation, prepared by Nicholas and coworkers [28,29]. Our group has recently reported two Co(II), *d*<sup>7</sup> complex salts: the homoleptic [Co{Ph(O)NN(O)Ph}<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>, with an unusually high coordination number of 8 and a distorted tetragonal coordination geometry, and the trigonal prismatic, heteroleptic [Co(bpy){Ph(O)NN(O)Ph}<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> [30], whose structures are shown in Fig. 1 and which have each been shown to selectively induce apoptosis in the SK-HEP-1 liver cancer cell line [31].

The possibility that azodioxides such as Ph(O)NN(O)Ph may behave as redox-active ligands is suggested by its significant  $\pi$ -delocalization, indicated by structural parameters both as a free molecule [32,33] and in complexes [26,27,29,30], as well as by the observation of redox-activity in complexes of nitrosoarenes (ArNO), the monomeric forms of aryl azodioxides Ar(O)NN(O)Ar [25]: complexes are known in which ArNO is best considered a neutral ligand [34], a radical monoanion (ArNO<sup>-</sup>) [34-37], or a dianion (ArNO<sup>2-</sup>) that may be thought of as a doubly deprotonated arylhydroxylamine [34,38]. However, none of the azodioxide complexes reported to date have been characterized electrochemically. This work describes electrochemical studies on [Co{Ph(O)NN(O)Ph}<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> and [Co(bpy){Ph(O)NN(O)Ph}<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> and interprets their electrochemical behavior in terms of metal- vs. ligand-based redox activity.

## 2. Experimental

Cobalt azodioxide complexes [Co{Ph(O)NN(O)Ph}<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> **1** and [Co(bpy){Ph(O)NN(O)Ph}<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> **2** were prepared as previously reported by our group [30]. Ferrocene (Fc) was purchased and used without purification. Electrochemical measurements were made using a Pine Instrument Company WaveNow potentiostat. A platinum disk working electrode, platinum wire counter electrode, and silver pseudo-reference electrode were used for simple CV measurements. Spectroelectrochemical measurements were made using a Pine Instrument Company platinum honeycomb electrode as the working electrode, and a Shimadzu UV-2600 spectrometer was used to acquire spectra. Potentials are reported relative to the Fc<sup>+</sup>/Fc couple. All CV and spectroelectrochemical measurements were obtained in dimethylformamide (DMF), degassed by sparging with nitrogen and dried by storage over activated 4 Å molecular sieves, with 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. Disk electrodes were cleaned between experiments by polishing with 0.3 μm Al<sub>2</sub>O<sub>3</sub>, followed by sonication and electrochemical

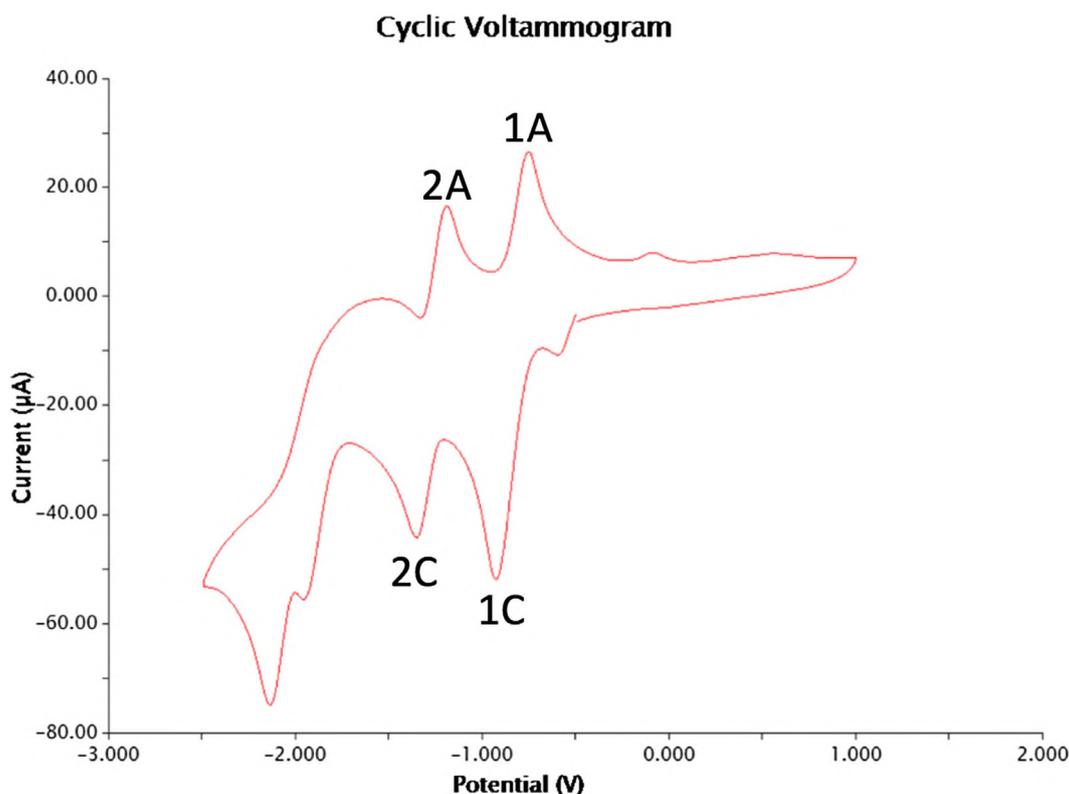


Fig. 2. Cyclic voltammogram of **1** with  $\nu = 100 \text{ mV s}^{-1}$ .

cleaning by continuous cycling between  $-1.5$  and  $1.5 \text{ V}$  in electrolyte solution. The honeycomb electrode was cleaned by immersion in “piranha solution” (30%  $\text{H}_2\text{O}_2$  and concentrated  $\text{H}_2\text{SO}_4$ ) for 5 min, followed by rinsing with distilled  $\text{H}_2\text{O}$  and air-drying. The spectroelectrochemical cell was cleaned by immersion in “piranha solution” (30%  $\text{H}_2\text{O}_2$  and concentrated  $\text{H}_2\text{SO}_4$ ) for 15 min, followed by rinsing with distilled  $\text{H}_2\text{O}$  and air-drying.

### 3. Results and discussion

A cyclic voltammogram (starting in the cathodic direction) of the homoleptic salt **1**, with a sweep rate of  $\nu = 100 \text{ mV s}^{-1}$ , is shown in Fig. 2 below. Two couples can be observed, the first of which, corresponding to cathodic peak 1C and anodic peak 1A in Fig. 2, has a peak potential separation of  $\Delta E_p = 84.7 \text{ mV}$  and a half-wave potential of  $E_{1/2} = -226 \text{ mV}$ . The second couple, corresponding to cathodic peak 2C and anodic peak 2A, has  $\Delta E_p = 115 \text{ mV}$  and  $E_{1/2} = -670 \text{ mV}$ .

CVs were obtained for sweep rates from  $100$  to  $500 \text{ mV s}^{-1}$ , and Randles-Sevcik plots of the cathodic and anodic peak currents,  $i_{p,c}$  and  $i_{p,a}$  respectively, vs.  $\nu^{1/2}$  were linear for both couples, indicating diffusion control [39], though the nonzero intercept indicates a non-faradaic contribution to the current [40]. The Randles-Sevcik plots for couples 1 and 2 are shown in Fig. 3 below. The cathodic and anodic peak potentials,  $E_{p,c}$  and  $E_{p,a}$  respectively, did not vary significantly with  $\nu$ , though the peak current ratio  $|i_{p,c}/i_{p,a}|$  varied from unity, likely due to the nonzero intercepts seen in the Randles-Sevcik plots. The average  $\Delta E_p$  and  $E_{1/2}$  values over all sweep rates examined, with standard deviations, are given in Table 1 below.

The CV of **1** in Fig. 2 shows additional, irreversible electrochemical behavior at more negative potentials. Partial resolution of these signals was accomplished by a single scan (starting in the cathodic direction) at low potential with a slow sweep rate of  $\nu = 10 \text{ mV s}^{-1}$ , as shown in Fig. 4. While the peaks are not completely distinct, two couples, corresponding to peaks 3A and 3C and peaks 4A and 4C in Fig. 4, can be tentatively identified, with  $E_{1/2}$  values of  $-1668.5 \text{ mV}$  and  $-1889 \text{ mV}$

estimated for couples 3 and 4, respectively.

A CV (starting in the cathodic direction) of the heteroleptic salt **2**, with a sweep rate of  $\nu = 100 \text{ mV s}^{-1}$ , is shown in Fig. 5 below. Two couples can be observed, the first of which, corresponding to cathodic peak 1C and anodic peak 1A in Fig. 4, has a peak potential separation of  $\Delta E_p = 40 \text{ mV}$  and a half-wave potential of  $E_{1/2} = -560 \text{ mV}$ . The second couple, corresponding to cathodic peak 2C and anodic peak 2A, has  $\Delta E_p = 116 \text{ mV}$  and  $E_{1/2} = -1018 \text{ mV}$ . The signal at more negative potentials is likely due to reduction of solvent and/or electrolyte at the Pt working electrode, as it was also observed during electrochemical cleaning of the electrode in blank electrolyte solution.

CVs were obtained for sweep rates from  $100$  to  $500 \text{ mV s}^{-1}$ , and Randles-Sevcik plots of the cathodic and anodic peak currents,  $i_{p,c}$  and  $i_{p,a}$  respectively, vs.  $\nu^{1/2}$  were linear for both couples (with the exception of an outlier at  $200 \text{ mV s}^{-1}$ ), again indicating diffusion control [39] with the nonzero intercept due to a non-faradaic contribution to the current [40]. The Randles-Sevcik plots for couples 1 and 2 are shown in Fig. 6 below. The cathodic and anodic peak potentials,  $E_{p,c}$  and  $E_{p,a}$  respectively, did not individually vary dramatically with  $\nu$ , but their difference  $\Delta E_p$  did gradually increase with increasing  $\nu$  for each couple, more notably for couple 1. As in the case of **1**, the peak current ratio  $|i_{p,c}/i_{p,a}|$  varied from unity, likely due to the nonzero intercepts seen in the Randles-Sevcik plots. The average  $\Delta E_p$  and  $E_{1/2}$  values, with standard deviations, over all sweep rates examined (excepting the outlier value at  $200 \text{ mV s}^{-1}$  for couple 1) are shown in Table 2 below.

The well-defined couples for complexes **1** and **2** discussed above are proposed to be quasireversible ( $E_q E_q$ ). While the peaks are well separated, the average  $\Delta E_p$  values are significantly greater than the  $58 \text{ mV}$  expected for truly reversible couples [39,41], with the exception of the first couple for **2**, which varies significantly with  $\nu$ . A gradual increase of  $\Delta E_p$  with  $\nu$  is predicted for quasireversible couples [39,42]. The quasireversibility of these couples may be due to dissociation of a  $\text{Ph(O)NN(O)Ph}$  (az) ligand (in **1** or **2**) or a  $\text{bpy}$  ligand (in **2**) upon reduction, similar to the results observed by Cabral, MacFarlane, and coworkers for  $\text{Co}(\text{bpy})_3^{2+}$  [17]. We do not propose that this dissociation is

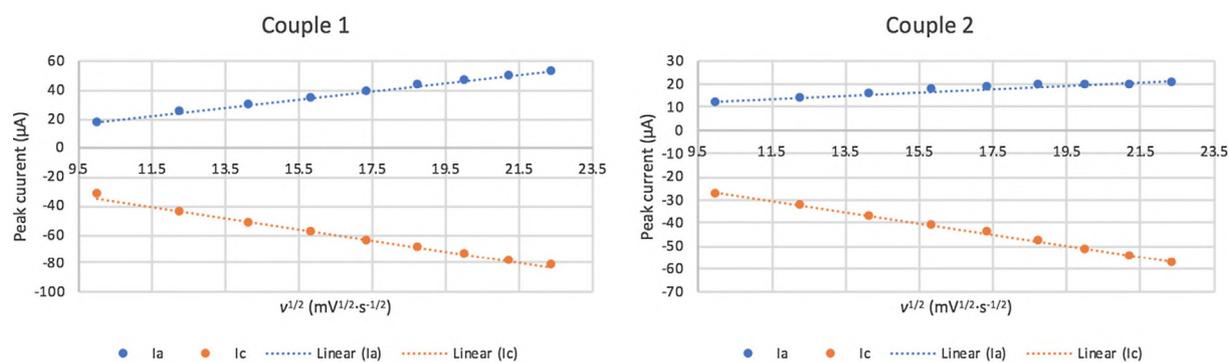


Fig. 3. Randles-Sevcik plots for **1**.

**Table 1**  
Average  $\Delta E_p$  and  $E_{1/2}$  values for **1**.

Redox couple	1	2
Average $\Delta E_p$ (mV)	$144 \pm 28$	$135 \pm 11$
Average $E_{1/2}$ (mV)	$-227 \pm 1$	$-664 \pm 3$

completely irreversible, as we do not see a linear dependence of peak potential on the logarithm of sweep rate, as is predicted for an  $E_qC_i$  reaction sequence [41,43]. Spectroelectrochemical experiments (*vide infra*) are also consistent with some degree of reversibility for both **1** and **2**.

In addition to these well-defined couples, the CV of **1** shows irreversible signals at more negative potentials, which can be partially resolved into two additional couples, as shown in Fig. 4. We propose that the well-defined, quasireversible couples of **1** (couples 1 and 2) correspond to  $\text{Co(II)/Co(I)}$  and  $\text{Co(I)(az)/Co(I)(az}^-)$ , where the second

reduction is azodioxide ligand-based. The less well-resolved couples (**3** and **4**) are proposed to consist of  $\text{Co(I)(az}^-)/\text{Co(0)(az}^-)$  and  $\text{Co(0)(az}^-)/\text{Co(-I)(az}^-)$ . The observed irreversibility of these reductions is proposed to be due to the decomposition of  $\text{Co(0)}$  to elemental  $\text{Co}$ , whose deposition on the working electrode may lead to the observed non-faradaic current, and the reaction of a  $\text{Co(-I)}$  species with protons derived from Hoffman elimination [44] of  ${}^t\text{Bu}_4\text{N}^+$ , yielding an unstable hydrido complex species.

We propose that the well-defined couples of **2** result from similar processes to those of **1**, where the first couple corresponds to  $\text{Co(II)/Co(I)}$  and the second to either  $\text{Co(I)(az)/Co(I)(az}^-)$  or  $\text{Co(I)(bpy)/Co(I)(bpy}^-)$ ; this second couple, if it corresponds to a ligand-based reduction, may plausibly involve reduction on either an azodioxide or bpy ligand.

The  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  couples with ligand loss observed by Cabral, MacFarlane, and coworkers occurred at more negative potentials ( $-1210$  to  $-1400$  mV) [17] than those observed for our complexes, which suggests that azodioxide dissociation is more likely than bpy

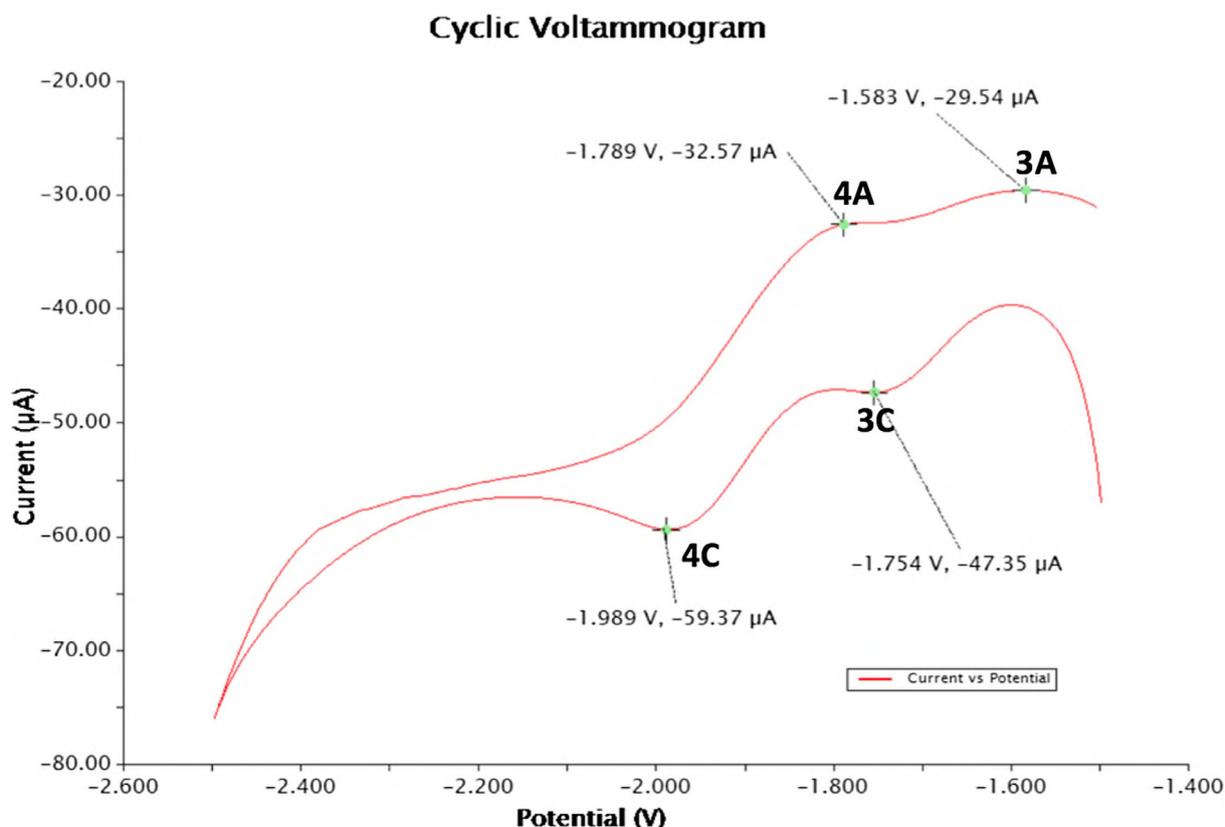


Fig. 4. Cyclic voltammogram of **1** at low potentials only with  $\nu = 10 \text{ mV s}^{-1}$  sweep rate.

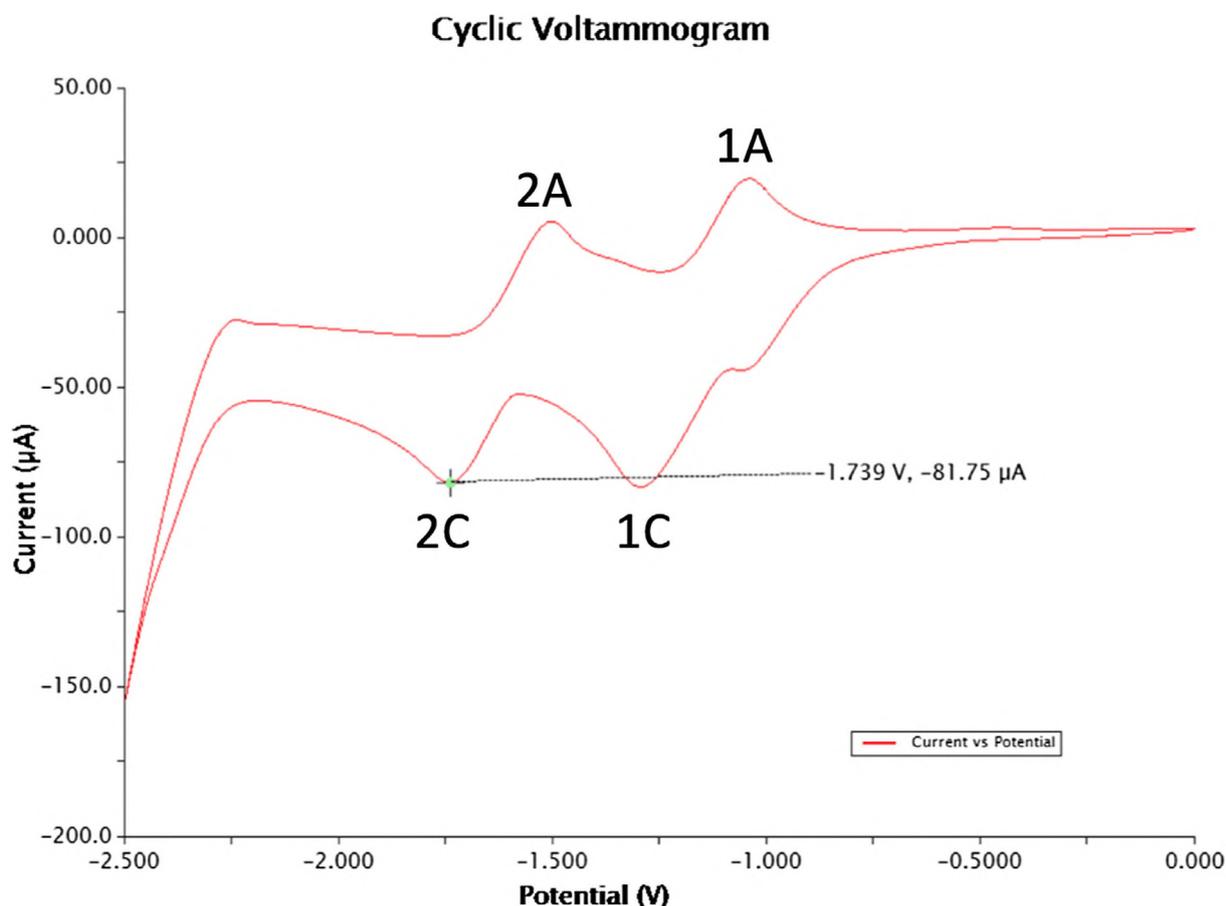


Fig. 5. Cyclic voltammogram of **2** with  $\nu = 100 \text{ mV s}^{-1}$ .

dissociation in the present case. The  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  couples observed by the groups of Conradie [14,15] and Fontecave [16] similarly occur at more negative potentials than observed for our complexes. We propose that the strongly electron-withdrawing nature of the azodioxide ligands makes reduction of our complexes more thermodynamically favorable than that of complexes with only ligands of the bpy, tpy, and phen families. It should be noted that an earlier report by Sawyer and coworkers [45] proposed that the one-electron reduction of  $\text{Co}(\text{bpy})_3^{2+}$  and two-electron reduction of  $\text{Co}(\text{bpy})_3^+$  in acetonitrile are both ligand-based, rather than metal-based. However, we are inclined to believe that the first reduction of our  $\text{Co}(\text{II})$  complexes is metal-based, given the results of recent DFT calculations by Conradie and coworkers on  $\text{Co}(\text{II})$  complexes of polypyridyl [14] and phenanthroline [15] ligands.

We performed UV-visible spectroelectrochemical measurements to shed further light on the redox changes observed. The absorbance

**Table 2**

Average  $\Delta E_p$  and  $E_{1/2}$  values for **2**.

Redox couple	1	2
Average $\Delta E_p$ (mV)	$68 \pm 22$	$135 \pm 12$
Average $E_{1/2}$ (mV)	$-567 \pm 4$	$-1016 \pm 2$

spectra of **1** at several potentials are shown (overlaid) in Fig. 7.

Fig. 7 shows that, before electrolysis, **1** displays peaks at 284 and 309 nm. Upon electrolysis at  $-2071.6 \text{ mV}$ , these peaks further overlap with each other, and two new peaks appear, at 228 and 432 nm. Upon reoxidation, the intensities of the peaks at 228 and 432 nm steadily decrease and those at 284 and 309 nm become resolved once again. By the time a potential of  $+928.4 \text{ mV}$  was reached, the absorption spectrum of the reaction mixture was very close to that observed before

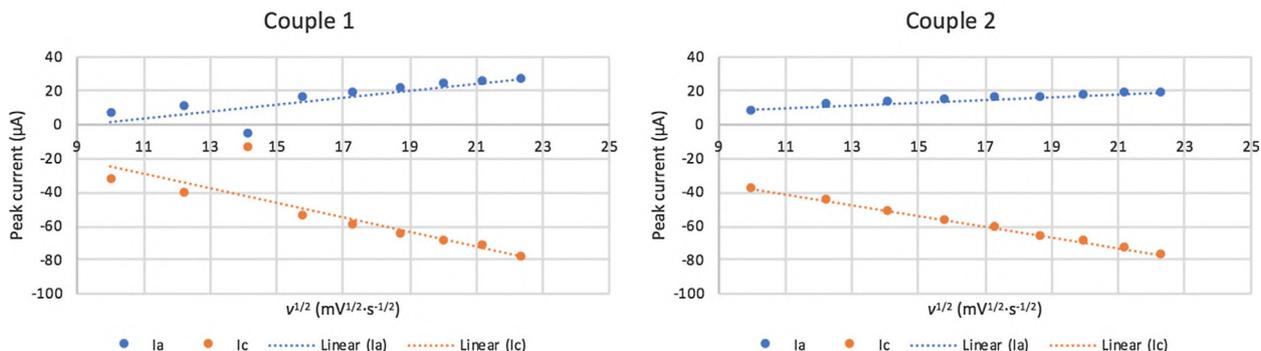


Fig. 6. Randles-Sevcik plots for **2**.

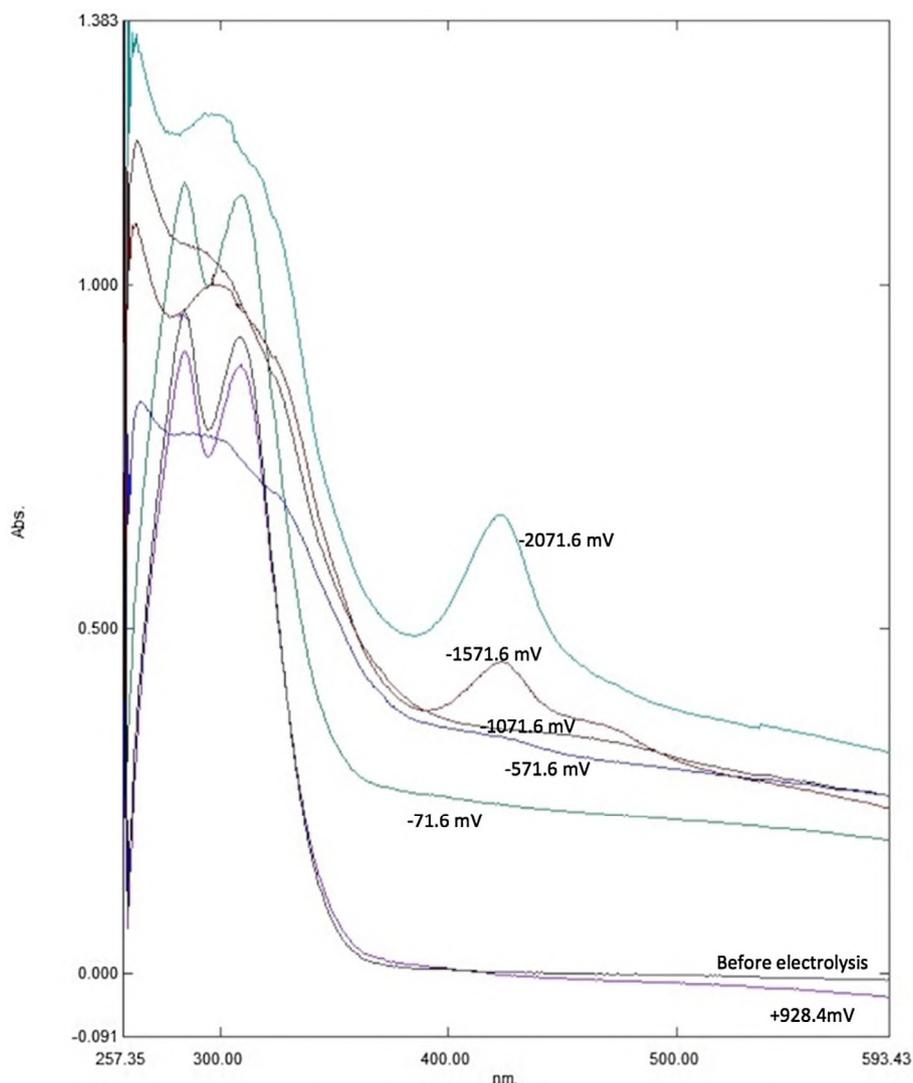


Fig. 7. Spectropotentiostatic analysis of **1** with potentials relative to Fc/Fc<sup>+</sup>.

electrolysis. The fact that the electrolysis seen here appears largely reversible on the experiment's time scale suggests that the reduced species is that formed in couple 2 (cf. Fig. 2 and Table 1), which as discussed earlier we propose to be [(Co<sup>+</sup>)(az)<sub>3</sub>(az<sup>-</sup>)], the result of a metal-based and a ligand-based reduction.

An analogous spectroelectrochemical experiment was run on **2**, with overlaid absorbance spectra shown in Fig. 8 below.

Fig. 8 shows that, before electrolysis, **2** displays a peak at 305 nm. Upon electrolysis at -2071.6 mV, this peak disappears and a new peak appears at 284 nm. Upon reoxidation, the peak at 284 nm gradually disappears and that at 305 nm reappears, though the 305 nm peak does not return to its initial intensity, even at a reoxidation potential of +1928.4 mV. This partial recovery of the initial spectrum is consistent with the quasireversibility observed for couples 1 and 2 in the CV of **2** (Fig. 5 and Table 2). We propose that formation of a doubly reduced species, either [(Co<sup>+</sup>)(bpy)(az)(az<sup>-</sup>)] or [(Co<sup>+</sup>)(bpy<sup>-</sup>)(az)<sub>2</sub>], gives rise to the peak at 283 nm, and that it undergoes some decomposition on the experiment's time scale, leading to incomplete recovery of **2** upon reoxidation. We believe that the doubly reduced species is more likely to be [(Co<sup>+</sup>)(bpy)(az)(az<sup>-</sup>)], with a reduced azodioxide ligand, as Heath and coworkers [46], in their spectroelectrochemical studies of Ru (bpy)<sub>3</sub><sup>2+</sup>, proposed that the doubly reduced form was [(Ru<sup>2+</sup>)(bpy)(bpy<sup>-</sup>)<sub>2</sub>], with a peak at 296 nm corresponding to a  $\pi \rightarrow \pi^*$  transition of the unreduced bpy ligand, fairly close to the 283 nm observed for

doubly reduced **2**, which we propose is due to its (unreduced) bpy ligand.

#### 4. Conclusion

Cathodic CV of cobalt azodioxide complexes **1** and **2** demonstrates two quasireversible couples for each species, proposed to correspond to reduction of Co(II) to Co(I), followed by reduction of a ligand to its radical anion form. The observed quasireversibility is proposed to be due to reduction-associated ligand dissociation. Irreversible peaks observed in the more negative region of **1** are proposed to arise from the deposition of elemental Co and the formation of unstable Co hydrido complexes. Spectroelectrochemical experiments on both **1** and **2**, consisting of reductive electrolysis followed by reoxidation, are consistent with the quasireversibility observed in the CV measurements. Future work will involve the use of coulometric techniques to further understand the nature of the reduction products, as well as computational modeling of **1** and **2** and their reduced forms.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

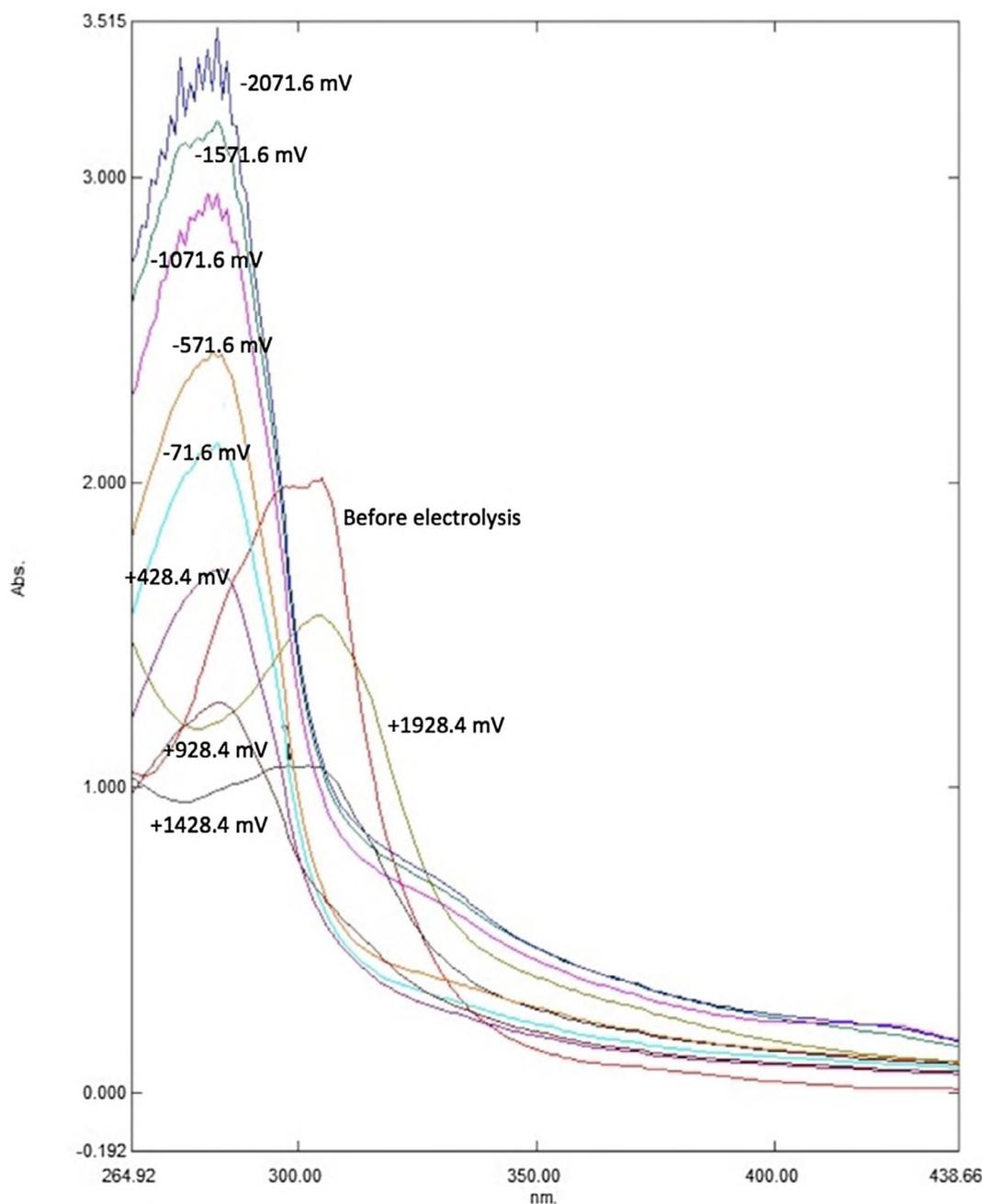


Fig. 8. Spectropotentiostatic analysis of **2** with potentials relative to  $\text{Fc}/\text{Fc}^+$ .

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