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Synthesis and Characterization of Cobalt(II) *N,N'*-Diphenylazodioxide Complexes

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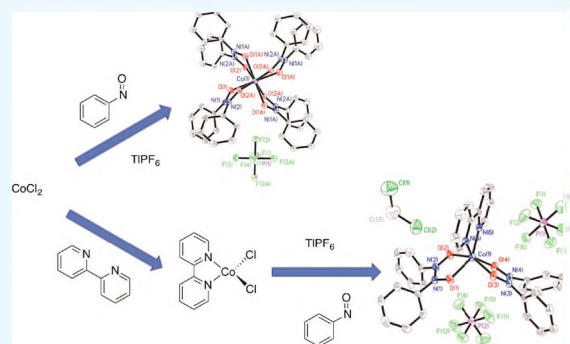
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Supporting Information

ABSTRACT: Removal of chloride from CoCl_2 with TIPF_6 in acetonitrile, followed by addition of excess nitrosobenzene, yielded the eight-coordinate cobalt(II) complex salt $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4](\text{PF}_6)_2$, shown by single-crystal X-ray analysis to have a distorted tetragonal geometry. The analogous treatment of the bipyridyl complex $\text{Co}(\text{bpy})\text{Cl}_2$ yielded the mixed-ligand cobalt(II) complex salt $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2](\text{PF}_6)_2$, whose single-crystal X-ray structure displays a trigonal prismatic geometry, similar to that of the iron(II) cation in the previously known complex salt $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3](\text{FeCl}_4)_2$. The use of TIPF_6 to generate solvated metal complex cations from chloride salts or chlorido complexes, followed by the addition of nitrosobenzene, is shown to be a useful synthetic strategy for the preparation of azodioxide complex cations with the noncoordinating, diamagnetic PF_6^- counteranion. Coordination number appears to be more important than *d* electron count in determining the geometry and metal–ligand bond distances of diphenylazodioxide complexes.

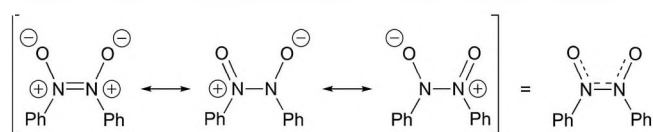


INTRODUCTION

In addition to nitric oxide itself,¹ organic derivatives of nitric oxide have been studied as ligands for transition metals.² Nitrosobenzene (PhNO), the prototypic nitrosoarene, exists as the dimer $\text{cis-Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ in the solid state but is primarily monomeric in solution.³ Nevertheless, solution-phase chemistry has been used to prepare complexes of metals with $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ as a chelating ligand. Structurally characterized examples include the Fe(II) complex cation salt $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3](\text{FeCl}_4)_2$, prepared by Nicholas and co-workers,⁴ and the Ca(II) complex salt $[\text{Ca}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}(\text{H}_2\text{O})_2(\text{THF})_3]_2$, from Hanusa and co-workers.⁵ In addition, Whiting and co-workers have prepared and characterized the related neutral Sc(III) diarylazodioxide complex $[\text{Sc}\{\text{Ar}(\text{O})\text{NN}(\text{O})\text{Ar}\}(\text{H}_2\text{O})_2(\text{OTf})_3]$, where $\text{Ar} = 2$ -methoxyphenyl and $\text{Tf} = \text{SO}_2\text{CF}_3$.⁶

Structural measurements of both free³ and Fe(II)-coordinated^{4b} $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ indicate significant π -delocalized character and suggest the possibility that it may behave as a redox-active ligand, such as 2,2'-bipyridyl (bpy)⁷ or the catecholate/semiquinone ligands studied by Pierpont and co-workers.⁸ Resonance structures of $\text{cis-Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ illustrating this delocalization are shown in Scheme 1.

Scheme 1. Resonance Structures of *cis-Ph*(O)NN(O)Ph



The presence of the paramagnetic Fe(III) anion FeCl_4^- in Nicholas' azodioxide complex salt $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3](\text{FeCl}_4)_2$ presented difficulties for the investigation of the cation's electronic structure via magnetic measurements or electron paramagnetic resonance spectroscopy.^{4b} As transition metal complexes of redox-active ligands have been used to catalyze a variety of organic reactions,⁹ we were motivated to investigate the synthesis of azodioxide complex cations with diamagnetic, redox-stable counteranions, both homoleptic species analogous to Nicholas' compound and heteroleptic complexes containing both $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ and the known redox-active ligand bpy.

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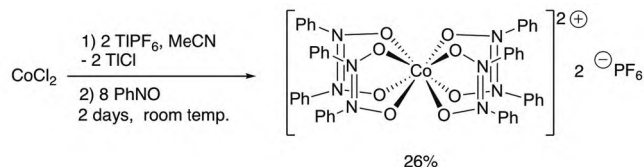
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RESULTS AND DISCUSSION

In hopes of isolating azodioxide complex cations with diamagnetic, redox-stable counteranions, we wished to remove Cl^- from the reaction mixture, to avoid the formation of paramagnetic complex anions with chlorido ligands, of the form MCl_x^y . Winfield and co-workers¹⁰ generated the salt $[\text{Fe}(\text{NCMe})_6](\text{PF}_6)_2$ by the treatment of FeF_2 with PF_5 in acetonitrile. Based on this result, we sought to prepare acetonitrile-solvated metal cations $\text{M}(\text{NCMe})_6^{2+}$ with the PF_6^- counterion *in situ* and then displace coordinated acetonitrile with diphenylazodioxide. In contrast to Winfield's strategy, we prepared $\text{M}(\text{NCMe})_6^{2+}$ by removal of Cl^- from chloride salts: suspensions of anhydrous metal chlorides MCl_2 ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) in acetonitrile were treated with stoichiometric amounts of TIPF_6 in solution to precipitate Cl^- as insoluble TlCl , followed by the addition of a PhNO solution with stirring to displace coordinated acetonitrile.

Thus far, Co is the only metal to yield a crystallographically characterizable azodioxide complex in this type of reaction: after stirring at room temperature for 12 to 48 h, filtration of the reaction mixture and removal of acetonitrile solvent from the filtrate *in vacuo*, followed by recrystallization from dichloromethane/hexane, yielded black crystals of the novel Co azodioxide complex $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4](\text{PF}_6)_2$ (Scheme 2). Based on UV–visible spectroscopy, some residual

Scheme 2. Synthesis of $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4](\text{PF}_6)_2$ 

PhNO (in the solid state, its dimer) remains after recrystallization, and elemental (CHN) analysis suggests the presence of a material with a lower mass percentage of carbon, likely $[\text{Co}(\text{NCMe})_6](\text{PF}_6)_2$. Traces of TlCl or TIPF_6 in the product may also result in lower mass percentages of carbon, hydrogen, and nitrogen, given the high atomic mass of thallium. A somewhat purer product, with CHN values closer to (though still notably different from) the theoretical ones, can be obtained by selecting the larger crystals formed in the recrystallization step, leaving behind the more powdery and less pure coprecipitate. Because of the presence of some impurities, the yield, molar absorptivities, and magnetic moment reported below for this compound are estimates only.

In contrast with Nicholas' six-coordinate, trigonal prismatic $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3]^{2+}$, the Co complex cation $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4]^{2+}$ is eight-coordinate, with a roughly tetragonal coordination geometry. A coordination number of 8 is very unusual for Co(II). The only monometallic, eight-coordinate Co(II) complexes thus far characterized are dodecahedral $(\text{Ph}_4\text{As})_2[\text{Co}(\text{NO}_3)_4]$, prepared by Bergman and Cotton,¹¹ dodecahedral $[\text{CoL}_2](\text{ClO}_4)_2$, where $\text{L} = 2,11$ -diazap[3.3](2,6)pyridinophane, prepared by Krüger and co-workers,¹² and the crown ether complex cations $[\text{Co}(12\text{-crown-4})_2]^{2+}$ and $[\text{Co}(\text{benzo-12-crown-4})_2]^{2+}$, prepared as salts of various polyiodide anions by Meyer and co-workers,¹³ both of which display square antiprismatic coordination.

The $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4]^{2+}$ cation has a distorted tetragonal coordination geometry, with idealized C_4 symmetry

assuming free N-phenyl bond rotation (Figure 1). Table 1 shows that the average N–N and N–O bond lengths in

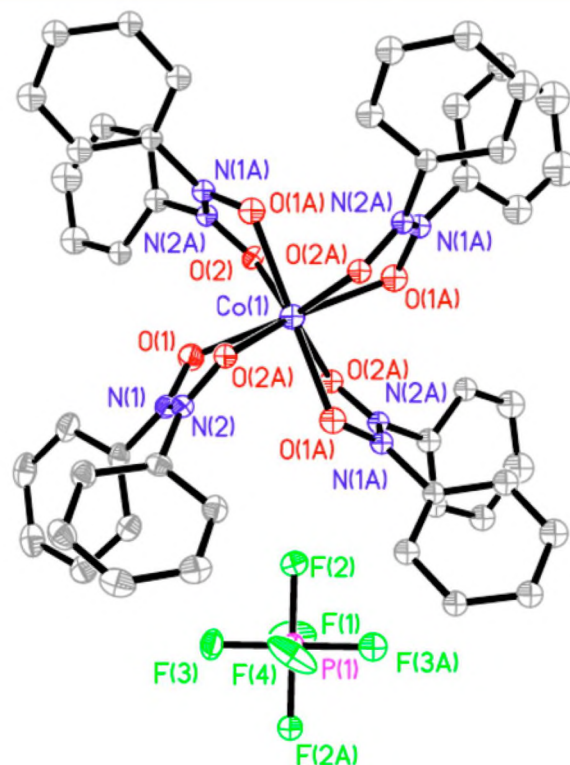


Figure 1. Thermal ellipsoid plot of $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4](\text{PF}_6)_2$, with thermal ellipsoids drawn to 50% probability and hydrogen atoms and one PF_6^- anion omitted for clarity.

Table 1. Metrical Parameters for $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ and Azodioxide Complexes^a

Compound	Mean N–N bond length (Å)	Mean N–O bond length (Å)	Mean M–O bond length (Å)	ref
Free az	1.32	1.27	N/A	3
$[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$	1.29	1.28	2.12	4b
$[\text{Co}(\text{az})_4](\text{PF}_6)_2$	1.31	1.28	2.24	This work
$[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$	1.31	1.28	2.10	This work
$[\text{Sc}(\text{az}')(\text{H}_2\text{O})_2(\text{OTf})_3]$	1.29	1.28	2.21	6
$[\text{Ca}(\text{az})(\text{H}_2\text{O})_2(\text{THF})_3]_2\text{I}_2$	1.30	1.27	2.42	5

^aAbbreviations: az = *cis*- $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$, az' = *cis*- $\text{Ar}(\text{O})\text{NN}(\text{O})\text{Ar}$, Ar = 2-methoxyphenyl, M = Ca, Sc, Fe, or Co.

$[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4]^{2+}$ are similar to those observed in free $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$, $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3]^{2+}$, and $[\text{Ca}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}(\text{H}_2\text{O})_2(\text{THF})_3]^{2+}$, though the N–N bond lengths in the complexes are slightly shorter than those in free $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$. The Co–O bond lengths in $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4]^{2+}$ are significantly longer than the Fe–O bond lengths in $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3]^{2+}$ but considerably shorter than the Ca–O (azodioxide) bond lengths in $[\text{Ca}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}(\text{H}_2\text{O})_2(\text{THF})_3]^{2+}$. The chelate rings in $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4]^{2+}$ are not planar, instead assuming a puckered “envelope” conformation with the Co atom lying outside of the

plane of the N and O atoms, in contrast to the Fe and Ca complexes, which both contain planar chelate rings.

The similarity in metrical parameters for free Ph(O)NN(O)Ph and Ph(O)NN(O)Ph coordinated to Fe or Co suggests that the electronic environment of this species does not vary drastically upon coordination. The significant difference in metal–ligand bond lengths between $[\text{Fe}\{\text{Ph(O)NN(O)Ph}\}_3]^{2+}$ and $[\text{Co}\{\text{Ph(O)NN(O)Ph}\}_4]^{2+}$ is thus proposed to be primarily due to steric, as opposed to electronic, reasons: the Co–O bonds are elongated to accommodate a larger number of ligands around the Co(II) center. The still greater Ca–O bond length in seven-coordinate $[\text{Ca}\{\text{Ph(O)NN(O)Ph}\}(\text{H}_2\text{O})_2(\text{THF})_3]^{2+}$ may reflect a greater ion-dipole component to the bonding of Ph(O)NN(O)Ph to an alkaline earth metal, compared to the greater covalent character of its bonding to transition metals with valence d orbitals.

The IR spectrum of $[\text{Co}\{\text{Ph(O)NN(O)Ph}\}_4](\text{PF}_6)_2$ is also indicative of similarities between free and bound Ph(O)NN(O)Ph . Lüttke¹⁴ studied the N–O stretching frequencies of azodioxides and found that aromatic *trans*-azodioxides display N–O stretching frequencies between 1248 and 1299 cm^{-1} , while aromatic *cis*-azodioxides display two N–O stretching frequencies each between 1342 and 1409 cm^{-1} . In our hands, the IR spectrum of solid *cis*- Ph(O)NN(O)Ph (obtained in ATR mode) shows a strong, broad band at 1390 cm^{-1} and two weaker bands at 1458 and 1485 cm^{-1} , the latter of which may be due to C–C stretching within the phenyl rings. In contrast, $[\text{Co}\{\text{Ph(O)NN(O)Ph}\}_4](\text{PF}_6)_2$ displays a somewhat less strong, broad band at 1370 cm^{-1} and weaker bands at 1460 and 1484 cm^{-1} . The similarity of the N–O stretching frequencies between free and bound Ph(O)NN(O)Ph is consistent with a fairly small effect of coordination on the electronics of the ligand. Further evidence for this small effect consists of the observation by Nicholas and co-workers^{4b} of bands at 1374, 1462, and 1481 cm^{-1} in the IR spectrum of $[\text{Fe}\{\text{Ph(O)NN(O)Ph}\}_3](\text{FeCl}_4)_2$.

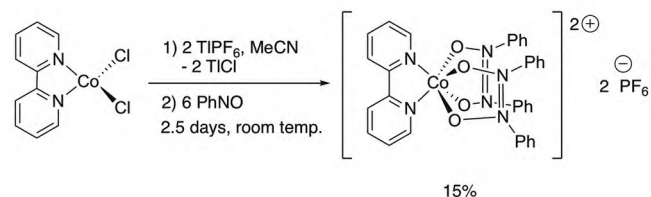
The UV–visible absorption spectrum of $[\text{Co}\{\text{Ph(O)NN(O)Ph}\}_4](\text{PF}_6)_2$ in acetonitrile shows peaks with λ_{max} values of 293 nm ($\epsilon = 4.03 \times 10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$) and 305 nm ($\epsilon = 4.62 \times 10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$). An additional peak with $\lambda_{\text{max}} = 282 \text{ nm}$ ($\epsilon = 5.36 \times 10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$) may be due to residual PhNO as an impurity, as the UV–visible spectrum of pure PhNO in acetonitrile displays a strong peak at this wavelength. Residual PhNO may also give rise to the peak at 285 nm in the UV–visible spectrum of $[\text{Fe}\{\text{Ph(O)NN(O)Ph}\}_3](\text{FeCl}_4)_2$ as measured by Nicholas' group.^{4b} The Beer–Lambert law plots for absorbance vs concentration at each peak wavelength were linear, suggesting that the Ph(O)NN(O)Ph ligands do not dissociate in solution to a significant extent, as such dissociation would be expected to be concentration-dependent.

The magnetic susceptibility of $[\text{Co}\{\text{Ph(O)NN(O)Ph}\}_4](\text{PF}_6)_2$ was measured at 22 °C, and an effective magnetic moment of 3.81 μ_{B} was calculated using the list of diamagnetic corrections compiled by Bain and Berry.¹⁵ This value is near the 3.87 μ_{B} predicted for a complex with three unpaired electrons assuming spin-only contributions to the magnetic moment, consistent with a Co(II) complex. The presence of some residual PhNO dimer, a diamagnetic compound, likely leads to a lower apparent magnetic moment than the true value for $[\text{Co}\{\text{Ph(O)NN(O)Ph}\}_4](\text{PF}_6)_2$.

After preparing the homoleptic azodioxide complex $[\text{Co}\{\text{Ph(O)NN(O)Ph}\}_4](\text{PF}_6)_2$, we sought to prepare a complex containing both Ph(O)NN(O)Ph and the known redox-active

ligand bpy. We chose the tetrahedral Co(II) complex $\text{Co}(\text{bpy})\text{Cl}_2$, whose preparation was reported by Iqbal and co-workers,¹⁶ as a synthon for a heteroleptic bpy/azodioxide complex. Treatment of this blue complex with 2 equiv of TIPF_6 in acetonitrile to remove Cl^- as insoluble TlCl , followed by addition of excess PhNO , yields the six-coordinate complex cation salt $[\text{Co}(\text{bpy})\{\text{Ph(O)NN(O)Ph}\}_2](\text{PF}_6)_2$ (Scheme 3).

Scheme 3. Synthesis of $[\text{Co}(\text{bpy})\{\text{Ph(O)NN(O)Ph}\}_2](\text{PF}_6)_2$



Filtration of the reaction mixture of Scheme 3, followed by removal of acetonitrile solvent *in vacuo* and recrystallization from dichloromethane/diethyl ether yielded garnet-red crystals of $[\text{Co}(\text{bpy})\{\text{Ph(O)NN(O)Ph}\}_2](\text{PF}_6)_2$ suitable for analysis by single-crystal X-ray diffraction. The crystal structure is shown in Figure 2.

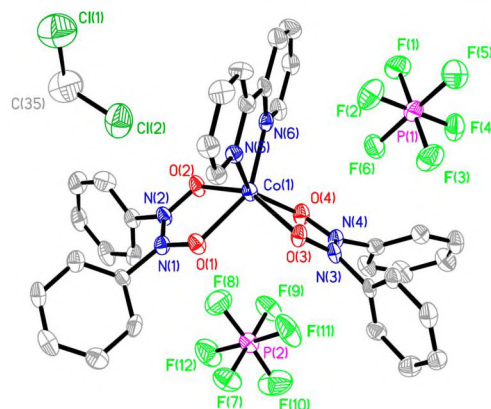


Figure 2. Thermal ellipsoid plot of $[\text{Co}(\text{bpy})\{\text{Ph(O)NN(O)Ph}\}_2](\text{PF}_6)_2$, with thermal ellipsoids drawn to 50% probability and hydrogen atoms removed for clarity. Molecules of the recrystallization solvent dichloromethane are present in the lattice.

We propose that the reaction proceeds by initial replacement of Cl^- by solvent to form $[\text{Co}(\text{bpy})(\text{NCMe})_n]^{2+}$, where $n = 2$ or 4, based on the immediate appearance of a peach color upon addition of TIPF_6 to the blue $\text{Co}(\text{bpy})\text{Cl}_2$. This is notably different from the light pink color observed upon addition of TIPF_6 to a solution of the simple salt CoCl_2 in acetonitrile, suggesting that bpy remains coordinated to the Co(II) center prior to the addition of PhNO .

The $[\text{Co}(\text{bpy})\{\text{Ph(O)NN(O)Ph}\}_2]^{2+}$ cation has a trigonal prismatic geometry, similar to $[\text{Fe}\{\text{Ph(O)NN(O)Ph}\}_3]^{2+}$, with idealized C_{2v} symmetry assuming free N–phenyl bond rotation. Table 1 shows that the N–N and N–O bond lengths in $[\text{Co}(\text{bpy})\{\text{Ph(O)NN(O)Ph}\}_2]^{2+}$ are similar to those in free Ph(O)NN(O)Ph and other diarylazodioxide complexes. Interestingly, the Co–O bond lengths in this complex are very close to the Fe–O bond lengths in $[\text{Fe}\{\text{Ph(O)NN(O)Ph}\}_3]^{2+}$, despite the differing d electron counts of the transition metals in these complexes: d^6 for

Fe(II) and d^7 for Co(II). However, the average metal–azodioxide oxygen bond length does increase significantly from these six-coordinate complexes to the seven-coordinate, d^0 complex $[\text{Sc}\{\text{Ar}(\text{O})\text{NN}(\text{O})\text{Ar}\}(\text{H}_2\text{O})_2(\text{OSO}_2\text{CF}_3)]$ and the eight-coordinate, d^7 complex $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4]^{2+}$. The number of crystallographically characterized azodioxide complexes remains small, thus making it difficult to determine a general trend, but from the limited number of structures known, coordination number, rather than metal or d electron count, seems to be the primary determinant of metal–ligand bond distance in azodioxide complexes, with the seven-coordinate, alkaline earth complex $[\text{Ca}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}(\text{H}_2\text{O})_2(\text{THF})_3]^{2+}$ an exception, as mentioned above.

The trigonal prismatic coordination geometry of $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2](\text{PF}_6)_2$ is very unusual for cobalt. Most previously reported monometallic, trigonal prismatic cobalt complexes contain complicated, hexadentate ligands, such as clathrochelates¹⁷ or pseudoclathrochelates.¹⁸ To the best of our knowledge, the only other structurally characterized trigonal prismatic cobalt complexes containing only bidentate ligands are the semiquinone complexes $\text{Co}(\text{NO}_2\text{phen})(3,6\text{-DBSQ})_2$ and $\text{Co}(\text{dafl})(3,6\text{-DBSQ})_2$, where 3,6-DBSQ = 3,6-di-*tert*-butylsemiquinone, NO_2phen = 5-nitro-1,10-phenanthroline, and dafl = 4,5-diaza-fluoren-9-one.^{8d}

Considerable experimental and theoretical work has been done on trigonal prismatic transition metal complexes, particularly d^0 species. The famous permethyl species $\text{W}(\text{CH}_3)_6$, whose synthesis was first reported in 1973,¹⁹ was initially proposed to display octahedral coordination geometry,²⁰ but its solid-state structure was later determined to be a distorted trigonal prism with C_{3v} symmetry.²¹ Its gas-phase structure was also shown to be a trigonal prism, with either C_{3v} or D_{3h} symmetry.²² The adoption of non-VSEPR trigonal prismatic geometries by six-coordinate d^0 complexes has been studied computationally at various levels of theory.²³

Albright and co-workers^{23a} developed a theoretical rationale for d^0 non-VSEPR structures, using the hypothetical CrH_6 molecule as a model system. They showed that, in the O_h geometry, the highest occupied molecular orbitals (HOMOs), t_{1u} -symmetry bonding combinations of metal p orbitals with hydrogen, are close in energy to the lowest unoccupied molecular orbitals (LUMOs), t_{2g} -symmetry nonbonding metal d_{xy} , d_{yz} , and d_{zx} orbitals. These two sets of frontier orbitals can mix via a second-order Jahn–Teller effect to yield a trigonal prismatic D_{3h} geometry, in which two occupied MOs are stabilized relative to O_h . Further distortion to C_{3v} symmetry allows for additional stabilization. While the calculations of Albright and co-workers predicted that a D_{3h} structure would be more stable for $\text{W}(\text{CH}_3)_6$ than C_{3v} , later calculations by Kaupp,^{23b} which accounted for electron correlation, did predict a ground-state C_3 structure for $\text{W}(\text{CH}_3)_6$, with the WC_6 heavy-atom skeleton displaying C_{3v} symmetry, consistent with experiment.²¹

The observed trigonal prismatic geometry of this compound and $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3](\text{FeCl}_4)_2$ may be understood in light of the fact that *cis*-azodioxides are isolobal, by the analogy of Hoffmann,²⁴ with dithiolene dianions $\text{R}_2\text{C}_2\text{S}_2^{2-}$. Transition metal tris(dithiolene) complexes $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3$, where M is a metal from group 5, 6, or 7, and which can be neutral, cationic, or anionic, are known to frequently display trigonal prismatic coordination,²⁵ and the relative energy orderings of their MOs are dependent on the identity of the metal and the charge of the complex, due to the heavily metal–ligand delocalized

character of the MOs. Depending on the metal and charge, a dithiolene ligand may be considered as the closed-shell dianion $\text{R}_2\text{C}_2\text{S}_2^{2-}$, the radical monoanion $\text{R}_2\text{C}_2\text{S}_2^-$, or the neutral, closed-shell species $\text{R}_2\text{C}_2\text{S}_2$. Similarly, one may envision that formally neutral $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ may behave, in certain complexes, as the radical monocation $[\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}]^+$ or the closed-shell dication $[\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}]^{2+}$. Theoretical studies of the electronic structures of $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3]^{2+}$ and $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2]^{2+}$ are currently in progress to clarify the character of $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$ in these complexes.

The infrared spectrum of $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2](\text{PF}_6)_2$ shows a set of overlapping peaks in the N–O stretching region,¹⁴ with greatest intensity at 1370 cm^{-1} , 1444 cm^{-1} , and 1478 cm^{-1} . It is similar in this respect to the IR spectra of free *cis*- $\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}$, $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4](\text{PF}_6)_2$, and $[\text{Fe}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_3](\text{FeCl}_4)_2$,^{4b} all of which display a strong peak between 1370 and 1390 cm^{-1} and two less intense peaks between 1458 and 1485 cm^{-1} , though for $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2](\text{PF}_6)_2$, the lowest-frequency peak in this region is no longer the most intense.

The UV–visible absorption spectra of $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2](\text{PF}_6)_2$ in acetonitrile show two peaks, with λ_{max} values of 246 nm ($\epsilon = 1.38 \times 10^4\text{ M}^{-1}\cdot\text{cm}^{-1}$) and 304 nm ($\epsilon = 2.26 \times 10^4\text{ M}^{-1}\cdot\text{cm}^{-1}$). The peak at 304 nm is in a very similar position to that observed for $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4](\text{PF}_6)_2$ at 305 nm and may reflect charge transfer between the Co center and the azodioxide. The peak at 246 nm likely corresponds to a bpy ligand-centered $\pi \rightarrow \pi^*$ transition, as the UV–visible spectra of free bpy in acetonitrile show a peak at 237 nm ($\epsilon = 2.78 \times 10^4\text{ M}^{-1}\cdot\text{cm}^{-1}$).

The magnetic susceptibility of $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2](\text{PF}_6)_2$ was measured at $22\text{ }^\circ\text{C}$, and an effective magnetic moment of $4.74\ \mu_{\text{B}}$ was calculated. This value is in the range of magnetic moments commonly observed for Co(II) complexes with three unpaired electrons.²⁶ An orbital angular momentum contribution to the magnetic moment is clearly present, as the spin-only magnetic moment predicted for a complex with three unpaired electrons would be only $3.87\ \mu_{\text{B}}$. Octahedral and tetrahedral Co(II) complexes are well-known to have substantial orbital angular momentum contributions to their magnetic moments,²⁷ and the trigonal prismatic Co(II) complex $[\text{Co}(\text{PccBF})](\text{BF}_4)$, where PccBF^- is the hexadentate ligand fluoroborotris(2-carboxaldoximo-6-pyridyl)phosphine, has been shown to have a solid-state magnetic moment of $4.91\ \mu_{\text{B}}$.²⁸

CONCLUSION

The eight-coordinate cobalt complex salt $[\text{Co}\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_4](\text{PF}_6)_2$ and the trigonal-prismatic $[\text{Co}(\text{bpy})\{\text{Ph}(\text{O})\text{NN}(\text{O})\text{Ph}\}_2](\text{PF}_6)_2$ have been prepared and structurally characterized. Theoretical work is in progress to gain further insight into the electronic structure of these new cobalt complexes with unusual coordination geometry. Further experimental work will focus on the examination of the mixed bpy/azodioxide complex for possible redox activity and catalytic ability.

METHODS

General Experimental Considerations. Unless otherwise indicated, operations were performed under anhydrous and anaerobic conditions (a dry nitrogen atmosphere), using

standard Schlenk line and glovebox (MBraun Labstar Pro) techniques. Glassware was dried in an oven at 160 °C prior to use. NMR spectra were acquired using a Bruker Avance III 400 MHz spectrometer. Infrared spectra data were recorded on a PerkinElmer Spectrum 2 spectrometer, with the samples as neat solids, in attenuated total reflectance (ATR) mode. UV–visible spectra were obtained in acetonitrile solution in gastight cuvettes (path length 1.2 cm) on a Shimadzu UV-2600 spectrometer. Magnetic susceptibility measurements were performed using a Sherwood Scientific MK 1 magnetic susceptibility balance. Elemental analysis was performed by Galbraith Laboratories, Inc. (Knoxville, TN). Nondeuterated solvents were deoxygenated by sparging with dry nitrogen and then dried via passage through activated alumina in an MBraun MB-SPS solvent purification system. CD₃CN was degassed via the freeze–pump–thaw method and dried over activated 4 Å molecular sieves. Reagents were obtained from commercial suppliers (Sigma-Aldrich, Fisher, Strem, TCI) and used without further purification.

Safety Note. These synthetic procedures involve the use of thallium(I) hexafluorophosphate (TlPF₆). Thallium compounds are highly toxic when ingested, inhaled, or absorbed through the skin. While the syntheses described are performed in a glovebox or sealed Schlenk tube, due to the air-sensitivity of nitrosobenzene and the cobalt complex products, extreme caution should be taken when disposing of thallium-containing waste material in a fume hood.

Synthesis of [Co{Ph(O)NN(O)Ph}₄](PF₆)₂. In the glovebox, 0.206 g (1.58 mmol) anhydrous CoCl₂ was suspended in 30 mL acetonitrile and stirred. To this stirred suspension was added a solution of 1.11 g (3.17 mmol) TlPF₆ in 5 mL acetonitrile. A white precipitate of TlCl was immediately observed, along with the appearance of a light pink color in solution. After 15 min, a solution of 1.30 g (12.1 mmol) PhNO in 20 mL acetonitrile was added, and the solution was stirred for 2 days at room temperature. The reaction mixture was then filtered through a fritted-glass funnel to remove TlCl, and solvent was removed from the filtrate under vacuum to yield the crude product. The crude product was dissolved in a minimal amount of dichloromethane and placed in the glovebox freezer at –30 °C overnight, after which some unreacted PhNO dimer crystallized. The supernatant was removed from the PhNO dimer crystals and transferred into another vessel. Hexane was gently layered on top of the supernatant, and the mixture returned to the freezer for an additional 2.5 days, yielding black crystals of [Co{Ph(O)NN(O)Ph}₄](PF₆)₂ suitable for X-ray diffraction. The crystals were removed with a spatula from a powdery coprecipitate and put under vacuum, yielding 0.50 g [Co{Ph(O)NN(O)Ph}₄](PF₆)₂ (0.41 mmol, 26%). UV–visible spectra in acetonitrile: λ_{max} (nm) (ε [M⁻¹·cm⁻¹]): 282 (5.36 × 10⁴), 293 (4.03 × 10⁴), 305 (4.62 × 10⁴). FT-IR spectrum (solid-phase): ν (cm⁻¹) 1484, 1460, 1370 (broad), 1167, 951, 833 (strong), 765, 690, 666, 557 (strong). Elemental analysis: 34.26% C, 2.79% H, 8.86% or 8.68% N (two measurements performed) (theoretical: 47.81% C, 3.34% H, 9.29% N).

Synthesis of Co(bpy)Cl₂. The procedure reported by Iqbal and co-workers¹⁶ was followed with minor modification. In the glovebox, 1.57 g (9.92 mmol) 2,2'-bipyridyl (bpy) was dissolved in 30 mL acetonitrile and stirred. To this stirred solution was added 1.28 g (9.86 mmol) solid anhydrous CoCl₂. The reaction mixture was stirred overnight at room temperature, during which time a blue precipitate formed. The solvent

was removed under vacuum, and the resulting blue powder was rinsed with diethyl ether and dried under vacuum to yield the blue solid Co(bpy)Cl₂ (0.74 g, 26%), used without further purification.

Synthesis of [Co(bpy){Ph(O)NN(O)Ph}₂](PF₆)₂. In the glovebox, 0.517 g (1.79 mmol) Co(bpy)Cl₂ was suspended in 50 mL acetonitrile and stirred. To this stirred suspension was added a solution of 1.31 g (3.75 mmol) TlPF₆ in 10 mL acetonitrile. A white precipitate of TlCl was immediately observed, concomitant with the appearance of a peach color in solution. After 15 min, a solution of 1.15 g (10.7 mmol) PhNO in 25 mL acetonitrile was added, and the mixture was stirred for 2.5 days at room temperature. Further color changes during the course of the reaction were not observed due to the deep green color of PhNO. The reaction mixture was then filtered through a fritted-glass funnel to remove TlCl, and solvent was removed from the filtrate under vacuum to yield the crude product. The crude product was dissolved in a minimal amount of dichloromethane and placed in the glovebox freezer at –30 °C for 1.5 days, after which point unreacted PhNO dimer crystallized. The supernatant was removed from the PhNO dimer crystals and transferred into another vessel. Diethyl ether was gently layered on top of the supernatant, and the mixture was returned to the freezer for 2.5 days, yielding garnet-red crystals of [Co(bpy){Ph(O)NN(O)Ph}₂](PF₆)₂ (0.25 g, 0.27 mmol, 15%). This paramagnetic complex does not give visible peaks in its ¹H NMR spectrum (CD₃CN). When such a spectrum is taken, small amounts of free PhNO can be seen, as was confirmed by spiking experiments in which additional PhNO was added to a sample of [Co(bpy){Ph(O)NN(O)Ph}₂](PF₆)₂. The level of this PhNO impurity is not large, as no signals for PhNO can be observed in the UV–visible or IR spectra under the peaks due to the main product. UV–visible spectra: λ_{max} (nm) (ε [M⁻¹·cm⁻¹]): 246 (1.38 × 10⁴), 304 (2.26 × 10⁴). FT-IR spectrum (solid-phase): ν (cm⁻¹) 3606 (broad), 3534 (broad), 2316, 2289, 1604, 1577 (weak), 1478, 1444, 1370 (broad), 1318, 1249 (weak), 1158, 1118 (weak), 1028, 954, 824 (strong), 766, 738, 689, 667, 652, 555 (strong). Elemental analysis: 38.81% C, 2.65% H, 10.29% N (theoretical: 43.75% C, 3.02% H, 9.00% N).

Spectral Analysis of PhNO. Commercial PhNO was analyzed by UV–visible spectroscopy in acetonitrile solution, and by IR spectroscopy in the solid state, for comparison with the spectra of the complexes [Co{Ph(O)NN(O)Ph}₄](PF₆)₂ and [Co(bpy){Ph(O)NN(O)Ph}₂](PF₆)₂. Note that solid “PhNO” is actually predominantly the dimer *cis*-Ph(O)NN(O)Ph, while in solution it exists predominantly as the PhNO monomer.³ UV–visible spectra in acetonitrile: λ_{max} (nm) (ε [M⁻¹·cm⁻¹]): 218 (1.25 × 10⁵), 237 (8.70 × 10³), 282 (1.69 × 10⁵). FT-IR spectrum (solid-phase): ν (cm⁻¹) 3064, 1485, 1458, 1390 (strong, broad), 1191, 1158, 950 (strong), 924, 777 (strong), 761 (strong), 689 (strong), 665 (strong), 616, 590, 490.

Spectral Analysis of 2,2'-Bipyridyl. Commercial 2,2'-bipyridyl was analyzed by UV–visible spectroscopy in acetonitrile, and by IR spectroscopy in the solid state, for comparison with the UV–visible and IR spectra of the complex [Co(bpy){Ph(O)NN(O)Ph}₂](PF₆)₂. UV–visible spectra in acetonitrile: λ_{max} (nm) (ε [M⁻¹·cm⁻¹]): 237 (2.78 × 10⁴), 275 (2.44 × 10⁴). FT-IR spectrum (solid phase): ν (cm⁻¹) 3055 (weak), 1739 (broad), 1578 (strong), 1558 (broad), 1451 (strong), 1415 (strong), 1250, 1139, 1084, 1054 (weak), 1040, 992, 894 (weak), 755 (strong), 653, 519 (strong).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01200.

Infrared spectra and crystallographic experimental details for all new compounds (PDF)

Crystallographic information files for [Co{Ph(O)NN(O)Ph}₄](PF₆)₂ (CCDC # 1811759) (CIF)

Crystallographic information files for [Co(bpy){Ph(O)NN(O)Ph}₂](PF₆)₂ (CCDC # 1823192) (CIF)

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Notes

The authors declare no competing financial interest.

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