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Metal–Halogen Secondary Bonding in a 2,5-Dichlorohydroquinonate Cobalt(II) Complex: Insight into Substrate Coordination in the Chlorohydroquinone Dioxygenase PcpA

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Despite the unprecedented selectivity of the hydroquinone ring-cleaving dioxygenase PcpA for *ortho*-chlorohydroquinones, there are no examples of an *ortho*-chlorohydroquinone bound to a transition-metal complex. Herein, the synthesis and characterization of $(\text{Tp}^{\text{Ph}_2}\text{Co})_2(\mu\text{-}2,5\text{-dichlorohydroquinonate})$, for which Tp^{Ph_2} is tris(3,5-diphenylpyrazolyl)borate, were explored. The dianionic 2,5-dichlorohydroquinonate bridges two $(\text{Tp}^{\text{Ph}_2}\text{Co})$ moieties and coordinates each cobalt(II) center through the oxygen and

chlorine atoms of the chlorohydroquinone. The Co–Cl distance of 2.778 Å shows the characteristics of a metal–halogen secondary bond, as we previously showed in *ortho*-halophenolate complexes. This compound represents the first example of metal–halogen secondary bonding with a halohydroquinone and, thus, provides a potential structural model for selective substrate binding to the metal center in PcpA.

Introduction

2,6-Dichlorohydroquinone 1,2-dioxygenase from *Sphingobium chlorophenicum* (PcpA) is a mononuclear non-heme iron(II)-containing ring-cleaving dioxygenase that displays unusual specificity for the binding of *ortho*-chloro- and *ortho*-bromohydroquinone substrates and *ortho*-chloro- and *ortho*-bromophenol inhibitors.^[1] It accomplishes the difficult cleavage of the aromatic ring during the multistep biodegradation of pentachlorophenol,^[2] a common pollutant.^[3] We hypothesized that the unusual specificity of PcpA for halogenated substrates may in part be due to a metal–halogen “secondary bond”.^[1] This type of metal–halogen interaction is known in coordination chemistry but is little studied. It results from the polarization of the electron shells of covalently bound halogen atoms, which pro-

duces a region of negative electrostatic potential around the equator and a region of positive potential at the pole.^[4] The positively charged crown of the polarizable halogen atom can interact with a Lewis base, which results in a halogen bond (Figure 1, right),^[5] whereas the negatively charged region near the equator can interact with the positive charge of a transition metal, which results in a metal–halogen secondary bond (Figure 1, left).^[6]

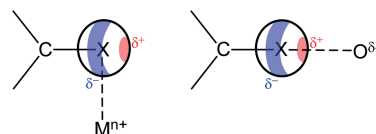


Figure 1. Illustration of the type of anisotropic charge distribution found for polarizable halogen atoms,^[4,5] which can lead to metal–halogen secondary bonding (left) or halogen bonding (right).

These metal–halogen secondary bonds have not been observed in any hydroquinone complexes but were recently characterized in complexes with *ortho*-chloro- and *ortho*-bromophenolates coordinated to divalent transition-metal ions,^[6b,7] including iron(II).^[7j,7k] In these complexes, the *ortho*-halophenolate binds as a bidentate ligand with the halogen atom occupying a coordination site on the metal. The length of the metal–halogen secondary bond can vary considerably, up to the normal metal–halide bond length plus 1 Å (Wulfsberg’s criterion).^[6b] We recently investigated

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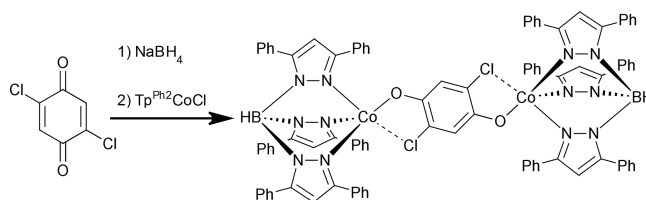
the strength of the metal–halogen interaction in the complex $\text{Tp}^{\text{Ph}_2}\text{Co}(2,6\text{-dcp})$ [2,6-dcp = 2,6-dichlorophenolate, Tp^{Ph_2} = tris(3,5-diphenylpyrazolyl)borate] by using variable-temperature NMR spectroscopy and found that the Co–Cl secondary interaction has a strength of about 30 kJ mol^{-1} ,^[7k] which is comparable to the strength of a hydrogen bond.^[8]

However, structurally characterized divalent metal complexes with untethered hydroquinonates that could model substrate binding are rare. Peters and Fiedler recently reported the first iron(II)–hydroquinonate complexes, but these lacked halogen substituents.^[9] The only other examples of untethered hydroquinonate complexes are for Mo, W, and Ru.^[10] Only one halohydroquinonate complex of any metal has been reported, in which tetrachlorohydroquinonate bridges between iron(III)–porphyrin moieties,^[11] but it lacks any *cis*-disposed site amenable to a biomimetic metal–halogen interaction. Herein, we report the first *ortho*-halohydroquinonate complex that exhibits metal–halogen secondary bonding, which demonstrates that this structural feature is reasonable to expect in substrate complexes of PcpA.

Results and Discussion

The facially capping tridentate ligand tris(3,5-diphenylpyrazolyl)borate (Tp^{Ph_2})^[12] was chosen to emulate the 2His-1Glu (or 3His) coordination to non-heme iron(II) that is highly conserved in ring-cleaving dioxygenases.^[13] Cobalt(II) was used rather than iron(II) to exploit its rich UV/Vis–near-IR absorption spectral features. A solution of 2,5-dichlorobenzoquinone in methanol was reduced and deprotonated with an excess amount of NaBH_4 (the same reducing agent as that used in the biological assays).^[1] UV/Vis absorption spectroscopy showed that the resultant species was the monoanionic 2,5-dichlorohydroquinonate ($2,5\text{diClHQ}^-$, $\lambda_{\text{max}} = 320 \text{ nm}$). After removal of the solvent, a solution of about 0.8 equiv. of $\text{Tp}^{\text{Ph}_2}\text{CoCl}$ ^[14] in chloroform was added, which yielded a dark brown solution

(Scheme 1). Filtration through Celite followed by removal of the solvent yielded a dark brown powder (95% yield). Alternatively, dark brown crystals were obtained by storage of the solution at -20°C for several days.



Scheme 1. Synthesis of $(\text{Tp}^{\text{Ph}_2}\text{Co})_2(2,5\text{diClHQ})$.

Single-crystal X-ray diffraction revealed a structure with two cobalt(II) centers bridged by a dianionic 2,5-dichlorohydroquinonate, $(\text{Tp}^{\text{Ph}_2}\text{Co})_2(2,5\text{diClHQ})$, in which the two $\text{Tp}^{\text{Ph}_2}\text{Co}$ units are related by a center of inversion (Figure 2). Each cobalt(II) center has a distorted trigonal bipyramidal geometry ($\tau = 0.66$),^[15] in which two pyrazole nitrogen atoms (N1 and N5) and the phenolate oxygen atom (O1) constitute the equatorial plane, and the remaining pyrazole nitrogen atom (N3) and the chlorine atom (Cl1) are axial. The Co–Cl distance is 2.778 \AA , which is only 0.567 \AA longer than the average cobalt–chloride covalent bond length for 10 four-coordinate $\text{Tp}^{\text{R,R'}}\text{CoCl}$ complexes (2.211 \AA)^[16] and 0.49 \AA longer than the average cobalt–chloride covalent bond length for 2 five-coordinate $\text{Tp}^{\text{Ph,Mc}}\text{Co}(\text{L})\text{Cl}$ complexes (2.29 \AA).^[16h,17] Thus, it clearly meets the distance criterion for a secondary bond.^[6b] The Co–Cl–C_{phen} angle is $92.26(13)^\circ$, which is close to the expected angle of 90° that would ideally position the region of negative electrostatic potential on the halogen atom to interact with the metal center.

The geometry of each cobalt(II) center in $(\text{Tp}^{\text{Ph}_2}\text{Co})_2(2,5\text{diClHQ})$ strongly resembles that of $\text{Tp}^{\text{Ph}_2}\text{Co}(2,6\text{-dcp})$, in which we experimentally determined the strength of the Co–Cl interaction to be about 30 kJ mol^{-1} (similar distorted trigonal bipyramidal geometry, $\tau = 0.72$), but with a Co–Cl distance that is shorter by 0.055 \AA .^[7k] The geometry also

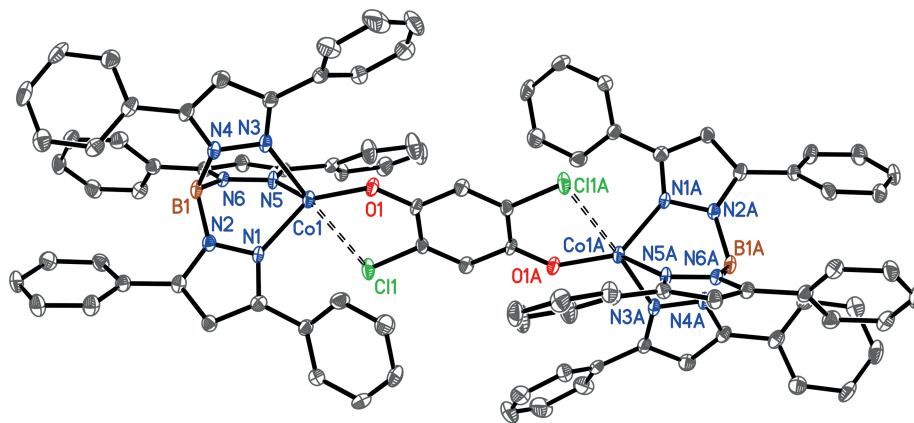


Figure 2. Molecular structure of $(\text{Tp}^{\text{Ph}_2}\text{Co})_2(2,5\text{diClHQ})$, with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Dashed lines represent the metal–halogen secondary interaction. Selected bond lengths [\AA] and angles [$^\circ$]: Co1–O1 $1.878(2)$, Co1–N1 $2.050(3)$, Co1–N3 $2.103(3)$, Co1–N5 $2.058(3)$, Co1–Cl1 $2.7781(12)$, O1–Co1–N1 $127.54(12)$, O1–Co1–N5 $136.77(12)$, N1–Co1–N5 $94.43(12)$, N3–Co1–O1 $99.96(11)$, N3–Co1–N1 $91.69(12)$, N3–Co1–N5 $87.09(12)$, Cl1–Co1–O1 $76.47(8)$, Cl1–Co1–N1 $90.01(9)$, Cl1–Co1–N5 $95.99(9)$, N3–Co1–Cl1 $176.36(9)$, Co1–O1–C46_{phen} $129.8(2)$, C47_{phen}–Cl1–Co1 $92.26(13)$.

strongly resembles that of the previously reported $(\text{Tp}^{\text{Ph}_2\text{Fe}})_2(2,5\text{diMeOHQ})$ complex (2,5diMeOHQ = 2,5-dimethoxyhydroquinone; $\tau = 0.59$),^[9a] in which the methoxy oxygen atom occupies the axial position analogous to the chlorine atom in the present complex, albeit at a shorter distance (2.328 Å). In contrast, the complex with an unsubstituted bridging hydroquinone, $[(\text{PhBP}^{\text{Ph}_3})\text{Fe}]_2(\mu\text{-hydroquinone})$, displays a more tetrahedral geometry about the iron(II) center, with P–Fe–P angles of 120–128°.^[9c] This further supports the presence of a Co–Cl secondary bond in the present complex and shows its influence on the geometry of the metal center.

The ¹H NMR spectrum of $(\text{Tp}^{\text{Ph}_2\text{Co}})_2(2,5\text{diClHQ})$ exhibits paramagnetically shifted signals typical of high-spin cobalt(II), with the pyrazole H4 resonance at $\delta = 62.0$ ppm (typical for TpCo^{II} complexes)^[7k] and a resonance at $\delta = 27.5$ ppm tentatively assigned as the 2,5diClHQ H3/H6 protons on the basis of its integration and large paramagnetic shift (Figure S1, see the Supporting Information). The UV/Vis–near-IR absorption spectrum (Figure 3) shows six major bands at energies of 29850, 22940, 18800, 15020, 12500, and 6860 cm^{-1} ($\lambda = 335, 436, 532, 666, 800,$ and 1457 nm).

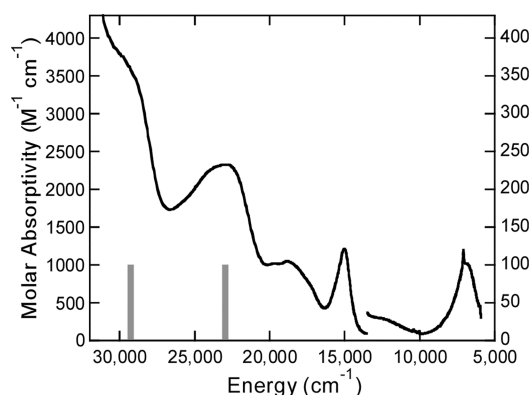


Figure 3. UV/Vis–near-IR absorption spectrum of $(\text{Tp}^{\text{Ph}_2\text{Co}})_2(2,5\text{diClHQ})$ in CHCl_3 at room temperature. The gray bars indicate the calculated energies of the hydroquinonate O $p\pi$ to Co d_{xy} charge-transfer and hydroquinonate ring $\pi \rightarrow \pi^*$ transitions.

Geometry optimization with ORCA^[18] by using the PBE0 functional^[19] gave excellent agreement with the experimentally determined structure, although it yielded a Co–Cl distance that was 0.072 Å too long, as previously seen with this functional for $\text{Tp}^{\text{Ph}_2\text{Co}}(2,6\text{-dcp})$ ^[7k] (see the Supporting Information for computational details). The Mayer bond order of the Co–Cl bond is 23–34% that of the Co–O/N bonds, which indicates that this is a weak interaction, again consistent with $\text{Tp}^{\text{Ph}_2\text{Co}}(2,6\text{-dcp})$. From time-dependent density functional calculations, the intense band at an energy of 22940 cm^{-1} in the UV/Vis–near-IR absorption spectrum ($\epsilon = 2450 \text{ M}^{-1} \text{ cm}^{-1}$) is assigned as the hydroquinonate-O $p\pi$ (HOMO) to cobalt(II) d_{xy} charge-transfer transition (see Figure S2 for contour surfaces of the orbitals). This is shifted to a lower energy by 3860 cm^{-1} relative to the same band for $\text{Tp}^{\text{Ph}_2\text{Co}}(2,6\text{-dcp})$,^[7k] owing to the higher energy of the O $p\pi$ orbital. The intense band at an

energy of 29850 cm^{-1} ($\epsilon = 3840 \text{ M}^{-1} \text{ cm}^{-1}$) is assigned as a hydroquinonate ring $\pi \rightarrow \pi^*$ transition. The remaining four bands are ligand field transitions of the cobalt(II) center at energies similar to those of $\text{Tp}^{\text{Ph}_2\text{Co}}(2,6\text{-dcp})$,^[7k] which is indicative of a similar ligand field environment. No hydroquinonate-O $p\sigma$ to cobalt(II) charge-transfer transition was predicted by time-dependent DFT in this energy range (the orbitals with O $p\sigma$ character are calculated to be $>20000 \text{ cm}^{-1}$ lower in energy than the O $p\pi$ orbital).

Given that $(\text{Tp}^{\text{Ph}_2\text{Co}})_2(2,5\text{diClHQ})$ contains the non-innocent 2,5-dichlorohydroquinone ligand bridging two transition metals, the electrochemical properties of this complex were examined. Cyclic voltammetry was performed on $(\text{Tp}^{\text{Ph}_2\text{Co}})_2(2,5\text{diClHQ})$ in chloroform with 0.1 M Bu_4NPF_6 as the supporting electrolyte (Figure 4). The cyclic voltammogram shows at least two irreversible oxidations occurring at positive potentials, with $E_{\text{pa}} = +0.01$ and $+0.42$ V versus the ferrocenium/ferrocene ($\text{Fc}^{+/0}$) couple. Similar complex electrochemical behavior was reported in iron(II)–hydroquinone complexes and were ascribed to both metal- and hydroquinone-based oxidation processes.^[9a,9b] The $(\text{Tp}^{\text{Ph}_2\text{Fe}})_2(2,5\text{diMeOHQ})$ complex exhibited a reversible oxidation at -0.57 V versus $\text{Fc}^{+/0}$, and it was shown to be hydroquinone based.^[9b] Given that cobalt(II) is expected to be oxidized at a considerably more positive potential than iron(II), we surmise that the oxidation events observed in the present complex are hydroquinone based. Neutral 2,5-diClHQ in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (1:1) undergoes irreversible oxidations at $+0.7$ and $+1.8$ V versus the saturated calomel electrode.^[20] The oxidation of the bridging 2,5-diClHQ²⁻ to the semiquinone form in the present complex at a potential of $+0.01$ V is consistent with the expectation that (1) dianionic 2,5-diClHQ²⁻ should be oxidized at a much less positive potential than the neutral form (as is seen with the bridging 2,5diMeOHQ²⁻), and (2) the more electron-poor chlorinated ring of 2,5diClHQ²⁻ should be oxidized at a more positive potential than 2,5diMeOHQ²⁻.^[21] The irreversible reduction at -0.72 V may be the reduction of cobalt(II).

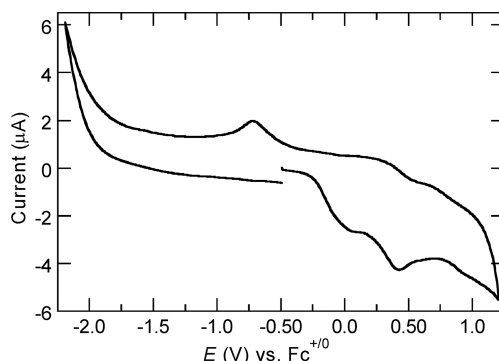


Figure 4. Cyclic voltammetry of $(\text{Tp}^{\text{Ph}_2\text{Co}})_2(2,5\text{diClHQ})$ in CHCl_3 with 0.1 M Bu_4NPF_6 as the supporting electrolyte at a scan rate of 200 mV s^{-1} . The irreversible oxidations at $E_{\text{pa}} = +0.01$ and $+0.42$ V are tentatively assigned as hydroquinone based.

It is notable that only the 2:1 $\text{Co}^{\text{II}}/2,5\text{diClHQ}^{2-}$ complex was formed, despite the fact that (1) 2,5-diClHQ was con-

firmed to be only singly deprotonated under the conditions used and (2) 2,5-diClHQ⁻ was in excess amount. Repeated attempts under varied conditions failed to yield an isolable 1:1 complex. We surmise that the greater acidity of 2,5-diClHQ (relative to the hydroquinones used in other metal complexes)^[21] may have favored the formation of the 2:1 bridging dianionic hydroquinonate complex. Given that this complex has a more highly charged ring than the monoanionic dihalophenolate complexes, it is notable that the same metal–halogen secondary interaction is observed here.

Conclusions

In summary, we successfully synthesized and characterized the first complex with an *ortho*-halohydroquinonate ligand coordinated to a divalent metal ion. The 2,5-dichlorohydroquinonate ligand coordinates in a bidentate fashion through a metal–halogen secondary bond, analogous to previously reported *ortho*-halophenolate complexes,^[7k] and with a slightly shorter Co–Cl distance. This provides a possible structural model for the binding of substrate to the active site of the enzyme PcpA and suggests that the metal–halogen interaction may play a role in its unusual specificity for *ortho*-chloro- and *ortho*-bromohydroquinones. It also indicates that metal–halogen secondary bonding may be a more general phenomenon than previously realized and could be designed into ligand coordination in a variety of applications. The complex undergoes at least two irreversible oxidation events at modest potentials, which most likely form an unstable semiquinone species. This is consistent with the proposed mechanism of PcpA,^[1] which requires formation of the semiquinone state, analogous to the generally accepted mechanism of the catechol extradiol dioxygenases.^[13c]

Experimental Section

General Considerations: CHCl₃ and CDCl₃ were dried with molecular sieves. All other reagents were reagent grade and were used without purification. The tris(3,5-diphenylpyrazolyl)borate ligand, KTp^{Ph2}, and Tp^{Ph2}CoCl were prepared by following literature procedures.^[12,14] All manipulations were performed under an N₂ atmosphere by using standard Schlenk techniques or in a glove box maintained at or below 1.0 ppm O₂. NMR spectra were collected with a Bruker Avance III 400 MHz spectrometer with a broadband probe. All signals in the NMR spectra of the complexes appeared as singlets and are reported in ppm. FTIR spectroscopy measurements were performed on KBr pellets and were acquired with a Perkin–Elmer Avatar 360. UV/Vis absorption spectra were acquired with a Cary 50 Bio UV/Vis spectrophotometer, and near-IR absorption spectra were acquired with a StellarNet InGaAs spectrophotometer. Solution spectra were acquired in quartz cuvettes of 1 cm optical path length. Cyclic voltammetry measurements were performed in a standard three-electrode cell configuration (working electrode, 3 mm diameter glassy carbon disk; counter electrode, Pt wire; reference electrode, Ag wire) by using a PAR 263A potentiostat. The solvent used was CHCl₃ with 0.1 M Bu₄NPF₆ as the supporting electrolyte, and the scan rate was

200 mV s⁻¹. The data are plotted versus the ferrocene/ferrocenium (Fc⁺⁰) couple measured under the same conditions. Elemental analysis was determined by the CENTC Elemental Analysis Facility at the University of Rochester. DFT calculations were performed on a model with the phenyl groups of the Tp^{Ph2} ligand replaced with methyl groups. Geometry optimization was performed with ORCA^[18] by using the PBE0^[19] functional and with the def2-SVP basis set for C and H atoms and the def2-TZVP basis set for all other atoms. Time-dependent DFT was performed with Gaussian 09 on the optimized structure obtained from ORCA by using the B3LYP^[22] functional and with the 6-311++G(d) basis set for Cl and the 6-311+G(d) basis set for all other atoms.

(Tp^{Ph2}Co)₂(μ-2,5-Dichlorohydroquinonate): 2,5-Dichlorobenzoquinone (12.2 mg, 0.069 mmol) was dissolved in methanol (10 mL) to produce a pale yellow solution. An excess amount of NaBH₄ was added to this solution until the solution became colorless, and the reaction proceeded until bubbling ceased. UV/Vis absorption spectroscopy showed that the resultant species was the monoanionic 2,5-dichlorohydroquinonate (2,5-diClHQ⁻, λ_{max} = 320 nm). The solvent was removed under reduced pressure to leave a white solid. A pale blue solution of Tp^{Ph2}CoCl (40.5 mg, 0.053 mmol) in chloroform (15 mL) was added to the reduced benzoquinone, and the mixture was then stirred for 45 min. A gradual color change to dark brown was observed. The mixture was filtered through Celite to leave a clear, dark brown solution. A dark brown powder was obtained by removal of the solvent under reduced pressure (42.8 mg, 95% yield). Alternatively, dark brown crystals were obtained from the solution in low yield by storage at –20 °C for several days. ¹H NMR (400 MHz, 25 °C, CDCl₃): δ = 62.0 (6 H, pz-H4), 27.6 (H3/H6, 2,5-diClHQ), 18.4 (2 H, BH), 13.1 (≈12 H, *o*/*m*-Ph), 12.6 (≈12 H, *o*/*m*-Ph), 10.8 (≈12 H, *o*/*m*-Ph), 9.20 (≈6 H, *p*-Ph), 9.08 (≈6 H, *p*-Ph), 8.84 (≈12 H, *o*/*m*-Ph) ppm. UV/Vis–near-IR (CHCl₃): λ_{max} (ε, M⁻¹cm⁻¹) = 335 (3840), 436 (2450), 532 (1030), 666 (1090), 800 (21), 1457 (101) nm. IR (KBr): ν̄ = 3060 (m), 2622 (w), 1546 (m), 1479 (s), 1456 (s), 1433 (m), 1415 (m), 1361 (m), 1212 (m), 1169 (s), 1078 (m), 1063 (m), 1010 (m), 857 (m), 839 (m), 760 (s), 695 (s), 668 (m), 570 (m) cm⁻¹. C₉₆H₇₀B₂Cl₂O₂N₁₂O₂·1/2(CHCl₃): calcd. C 68.43, H 4.20, N 9.92; found C 68.90, H 4.14, N 9.94.

CCDC 1413725 contains 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.

Supporting Information (see footnote on the first page of this article): Details of the X-ray crystallographic data collection and refinement and density functional theory calculations.

Acknowledgments

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