

Synthesis, Characterization, and the N Atom Transfer Reactivity of a Nitridochromium(V) Complex Stabilized by a Corrolato Ligand

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Cite This: *ACS Omega* 2022, 7, 28138–28147



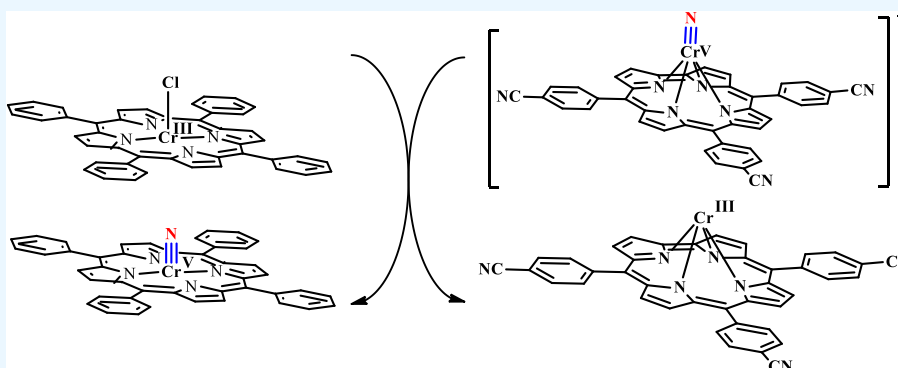
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ABSTRACT: Metal complexes bearing nitrido ligands ($M\equiv N$) are at the forefront of current scientific research due to their resemblances with the metal complexes involved in the nitrogen fixation reactions. An oxo(corrolato)chromium(V) complex was used as a precursor complex for the facile synthesis of a new nitrido(corrolato)chromium(V) complex. The nitrido(corrolato)chromium(V) complex was characterized by various spectroscopic techniques. Density functional theory (DFT) calculations were performed on the nitrido(corrolato)chromium(V) complex to assign the vibrational and electronic transitions of this complex. The chromium–nitrogen (nitrido) bond distance obtained in the DFT-optimized structure is 1.530 Å and matches well with the earlier reported authentic $Cr\equiv N$ bond distances obtained from the single-crystal X-ray diffraction data. This nitrido(corrolato)chromium(V) compound exhibited a sharp Soret band at 438 nm and a Q band at 608 nm. DFT calculations deliver that the origin of the bands at 438 and 608 nm is due to the intraligand charge transfer transitions. The nitrido(corrolato)chromium(V) complex showed one reversible oxidation and one reversible reduction couple at +0.53 and -0.06 V, respectively, vs the Ag/AgCl reference electrode. The simulation of the electron paramagnetic resonance data of the nitrido(corrolato)chromium(V) compound provided the following parameters: $g_{iso} = 1.987$, $A^{53}Cr = 26$ G, and $A^{14}N = 2.71$ G. From all these analyses, we can conclude that the electronic configuration in the native state of nitrido(corrolato)chromium(V) can be best described as $[(cor^{3-})Cr^V(N^{3-})]^-$. Reactions of nitrido(corrolato)chromium(V) with the chloro(porphyrinato)chromium(III) complex resulted in a complete intermetal N atom transfer reaction between chromium corrole and chromium porphyrin complexes. A second-order rate constant of 4.29 ± 0.10 $M^{-1} s^{-1}$ was obtained for this reaction. It was also proposed that this reaction proceeds *via* a bimetallic μ -nitrido intermediate.

INTRODUCTION

Synthetic metalloporphyrins are frequently described as model systems for various enzymatic active sites.¹ However, it was observed that often, these intermediates bearing metalloporphyrins are highly reactive, and thus, it essentially precludes their spectroscopic characterization. In this context, a corrole ligand system has some definitive advantage over the porphyrin-based systems.² Corrole is an 18 π -electron tetrapyrrolic aromatic system similar to porphyrin. It has a smaller cavity size than porphyrin and is also less symmetric than porphyrin.² Corroles are trianionic when fully deprotonated as opposed to porphyrin, which is dianionic.² The inner π system of corrole is more electron-rich, and thus, it stabilizes

the higher oxidation states of metals.^{3–26} Transition metal complexes bearing multiple bonds between metals and ligands, e.g., nitrido, imido, oxo, alkylidyne, and alkylidene, have gained considerable research interest in recent times.^{27–31} Multiple bonded metal–ligand complexes are frequently invoked in the atom and group transfer reactions. In this context, metal

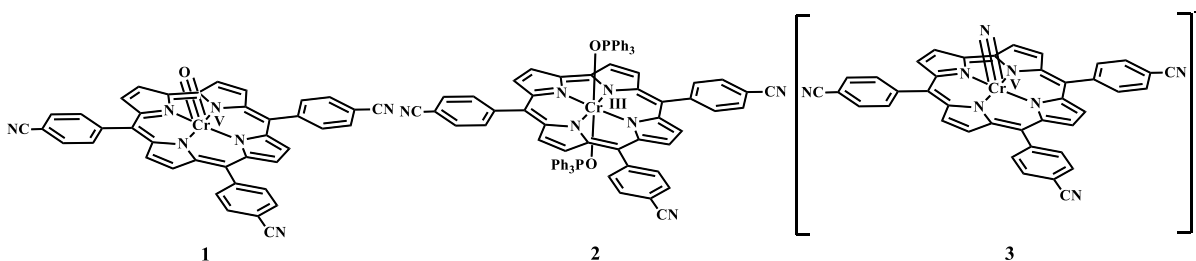
Received: April 12, 2022

Accepted: July 19, 2022

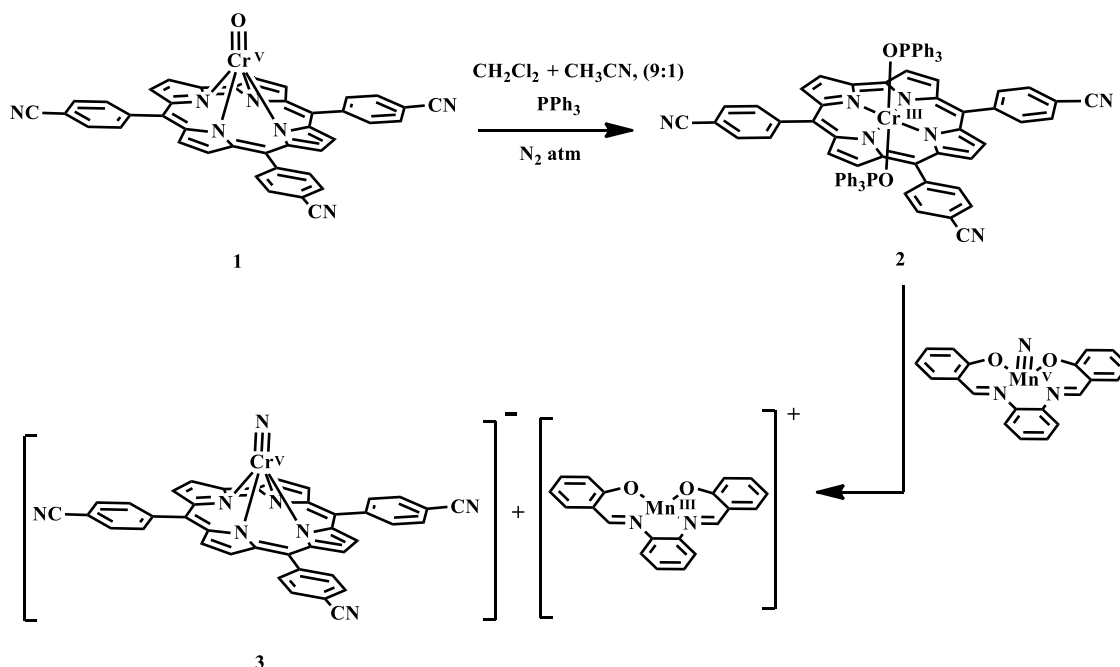
Published: August 3, 2022



Scheme 1. Structures of Oxo[5,10,15-tris(*p*-cyanophenyl)corrolato]chromium(V),³⁹ **1, {Bis(triphenylphosphineoxide)}[5,10,15-tris(*p*-cyanophenyl)corrolato]chromium(III), **2**, and [Nitrido{5,10,15-tris(*p*-cyanophenyl)corrolato}chromium(V)]⁻, **3****



Scheme 2. Schematic Representation of the Formation of Nitrido(corrolato)chromium(V), **3, from the Precursor Complex Oxido(corrolato)chromium(V), **1**, via the Intermediate Complex {Bis(triphenylphosphineoxide)}(corrolato)chromium(III), **2****



complexes bearing nitride ligands ($M\equiv N$) are at the forefront of current scientific research due to their resemblance with the metal complexes involved in the nitrogen fixation reactions.^{32,33} Nitride complexes are also efficiently used in the nitrogenation reactions of various organic compounds.^{34,35} The nitride ligand is also known for the stabilization of higher oxidation states of metals. Thus, a combination of nitride and corrole ligand functionalities would be a perfect choice for stabilizing higher oxidation states of metals. Metal complexes bearing highly oxidized metal centers are frequently encountered in various catalytic oxidation reactions.^{1,2} It was also observed that the metal complexes bearing a nitride ligand (N^{3-}) are more abundant with second- and third-row transition metals.³⁶ However, similar complexes with first-row transition metals are scarcely reported in the literature. Only a limited number of examples are available for well-characterized nitridochromium complexes {both (+V) and (+VI) oxidation states}.³⁷ It was also observed that similar reports in porphyrinoid-based ligand scaffolds, i.e., nitrido-(porphyrinoid)chromium(V/VI)-type complexes, are indeed very few.³⁸ The first structurally characterized nitrido-(porphyrinato)chromium(V) complex was reported by Groves *et al.*^{38a} In the corrole framework, spectroscopically charac-

terized nitrido(corrolato)chromium(V) complexes were reported by Gross and Golubkov^{38b} and Christensen *et al.*^{38c} We have reported here the synthesis of a new nitrido(corrolato)chromium(V) complex, namely, [nitrido{5,10,15-tris(*p*-cyanophenyl)corrolato}chromium(V)]⁻, **3** (Scheme 1). An oxo[5,10,15-tris(*p*-cyanophenyl)corrolato]chromium(V) complex, **1**,³⁹ has been used as a precursor complex, and the synthesis of a new nitrido(corrolato)chromium(V) complex was achieved *via* using nitrido(salophen)manganese(V) [salophen = *N,N'*-*o*-phenylenebis(salicylidene-iminato) dianion] as a nitrogen atom transfer reagent (Scheme 2). The nitrido{5,10,15-tris(*p*-cyanophenyl)corrolato}chromium(V) complex, **3**, has been fully characterized *via* various spectroscopic techniques. Theoretical calculations were also performed in order to understand the spectroscopic nature of this nitrido(corrolato)chromium(V) complex, **3**.

RESULTS AND DISCUSSION

Synthesis and Characterization. The oxo[5,10,15-tris(*p*-cyanophenyl)corrolato]chromium(V) complex (**1**) was synthesized by refluxing a mixture of 5,10,15-tris(*p*-cyanophenyl)corrole and $Cr(CO)_6$ in toluene by following an earlier reported protocol.³⁹ The elemental analyses and UV–Vis, FT–

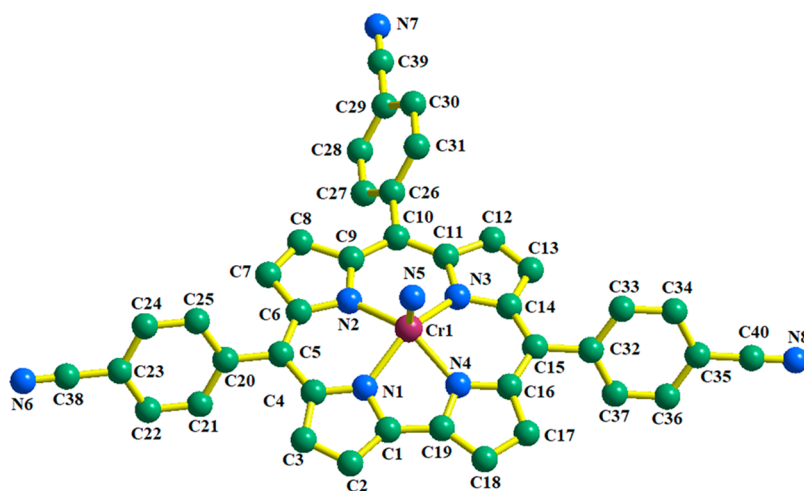


Figure 1. DFT-optimized structure of 3.

IR, and ESI-MS data (Figures S1–S3 and Tables S1 and S2) of complex 1 match well with the authentic compound reported in the literature.³⁹ Meanwhile, most often, the (corrolato)-chromium(III) complexes were used as a starting material and are converted into nitrido(corrolato)chromium(V) complexes *via* nitrogen atom transfer reactions using (salen)Mn^V(N) {salen = *N,N'*-ethylenebis(salicylideneiminato) dianion} or (saloph)Mn^V(N) complexes as a nitrogen atom source.^{38b} However, in the present case, we have used an oxo(corrolato)-chromium(V) complex as the precursor complex. We believe that the use of the oxo(corrolato)chromium(V) complex as a starting material will be more advantageous as the chromium metalation in the corrole core often yields the oxo(corrolato)-chromium(V) complex directly *via* aerial oxidation. Thus, one does not need to reduce it further in a separate reaction to get the precursor complex, (pyridine)₂(corrolato)chromium(III), as described by Gross and Golubkov.^{38b} We have observed that the addition of (saloph)Mn^V(N) and PPh₃ in a solution of the oxo(corrolato)chromium(V) complex in a dichloromethane–acetonitrile mixture in a stepwise manner resulted in the generation of the nitridochromium(V) complex in good yields (Scheme 2). Meanwhile, Gross *et al.* reported earlier the generation of (corrolato)Cr^{III}(OPPh₃)₂ derivatives *via* the treatment of PPh₃ into a solution of the oxo(corrolato)-chromium(V) derivative in an argon atmosphere.⁴⁰ Based on their observations, we have also proposed the generation of (corrolato)Cr^{III}(OPPh₃)₂ derivatives in the first step. Thus, the first step likely involves the reduction of the oxo(corrolato)-chromium(V) complex into the chromium(III)–corrolato complex with two axially bound O=PPh₃ ligands. This chemical transformation is highly feasible as it was observed earlier that oxo(corrolato)chromium(V) complexes can effectively transfer oxygen atoms to PPh₃ ligands and can generate (corrolato)chromium(III) and O=PPh₃.⁴⁰ The conversion of PPh₃ to O=PPh₃ was described by earlier researchers. We have also confirmed it *via* ESI-MS data. The intermediate compound, {5,10,15-tris(*p*-cyanophenyl)corrolato}Cr^{III}(OPPh₃)₂, 2 is highly unstable and is immediately converted back into the oxo(corrolato)chromium(V) derivative *via* aerial oxidation.

Albeit a different reaction condition was used, the similar reactivities of (corrolato)Cr^{III}(OPPh₃)₂ derivatives {corrolato = tris(pentafluorophenyl)corrolato} were earlier reported by Gross *et al.*⁴⁰ As these derivatives are highly air-sensitive, thus,

they have not isolated them in a pure form. We have also observed similar kinds of reactivities of this intermediate compound, 2. Compound 2 was characterized *via* the ESI-MS technique (Figure S5, see the Supporting Information). This intermediate compound, 2, was also analyzed *via* various spectroscopic techniques like UV–Vis, IR, and EPR (Figures S6–S8, see the Supporting Information). All these techniques prove the composition of compound 2. In the subsequent step, the nitrogen atom transfer took place (Scheme 2). The resultant nitrido(corrolato)chromium(V) derivative, 3, is paramagnetic in nature; thus, it is characterized *via* X-band EPR spectroscopy. Compound 3 is sufficiently stable in the solid state (for days).

However, in solution (except CH₃CN and benzene), the compound decomposes within minutes.

DFT-Optimized Structure. In order to support the experimental findings, we have performed the DFT calculations on [nitrido{5,10,15-tris(*p*-cyanophenyl)corrolato}chromium(V)][−], 3. As no crystal structure was reported earlier with other analogous nitrido(corrolato)chromium(V) complexes, thus, the bond parameters of the DFT-calculated structures can be compared with the literature-reported crystal structure of the nitrido(porphyrinato)chromium(V) derivative by Groves *et al.*^{38a} The bond lengths and angles of the DFT-optimized structure of 3 (Figure 1) match well with the earlier reported nitrido(porphyrinato)chromium(V) derivative.^{38a} The chromium–nitrogen (nitrido) bond distance obtained in the DFT-optimized structure of 3 is 1.530 Å. In the single-crystal data of nitrido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(V), CrN(TTP), the similar distance was reported to be 1.565 Å.^{38a} This short chromium–nitrogen (nitrido) bond distance supports triple bond formation between chromium and nitrogen. The out-of-plane displacement (from the N4 corrole plane) of the chromium atom is 0.577 Å. This displacement is comparable to the other literature-reported oxo(corrolato)chromium(V) derivatives.²³ In the oxo[10-(*p*-hydroxyphenyl)-5,15-bis(*m*-bromophenyl)corrolato]chromium(V) derivative, the chromium atom is axially displaced from the N4 corrole plane by 0.57 Å.²³

The chromium–nitrogen (pyrrolic) bond lengths are in the range of 1.988–1.997 Å. These bond distances matched nicely with the previously reported bond distances of CrN(TTP). The analogous distances in CrN(TTP) are in the ranges of 2.032–2.052 Å.^{38a}

Electronic Absorption Spectroscopy. Compound **1** exhibited a Soret band and a Q band at 404 and 557 nm, respectively. Compound **3** also exhibited a Soret band and a Q band at 438 and 608 nm, respectively. Two weak shoulders were also observed at 506 and 540 nm. Thus, both the Soret and Q bands are redshifted in the nitrido(corrolato)chromium(V) complex in comparison to the oxo(corrolato)chromium(V) complex. To support the experimentally obtained UV–Vis spectra, TD-DFT calculations were carried out on **3**. The theoretically calculated UV–Vis spectra of **3** match reasonably well with the DFT-calculated spectra (Figures 2 and 3). From

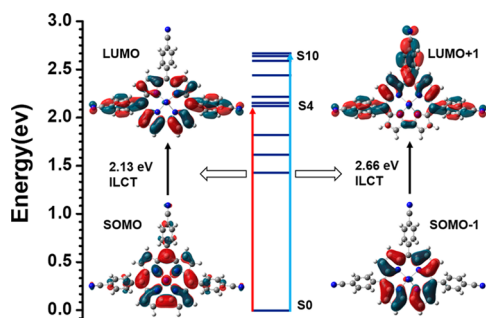


Figure 2. Calculated single occupied molecular orbitals (SOMO) and the lowest unoccupied molecular orbitals (LUMO) of **3** involved in particular electronic transitions with maximum contributions and their corresponding transition energies.

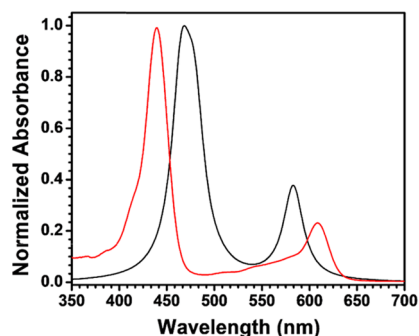


Figure 3. Experimentally obtained UV–Vis absorption spectrum (red line) of **3** and TD-DFT-based absorption spectrum (black line) of **3** in acetonitrile using an IEF-PCM solvent model (Lorentzian broadening with an FWHM of ~ 25 nm).

TD-DFT, the origin of the band at 466 nm, which matches with the experimentally observed absorption maximum at 438 nm, can be ascribed to SOMO-1 to LUMO+1 transitions (2.66 eV). The experimentally observed Q band at 608 nm is due to SOMO to LUMO transitions (2.13 eV). Further, the origins of the bands at 438 and 608 nm are attributed to the ILCT transitions (Figure 2). Selected molecular orbitals involved in the electronic transitions and their orbital contributions are given in Table S3 and Figure S9. It was also observed that the experimentally obtained FT-IR and FT-Raman spectra of **3** match well with the DFT-calculated FT-IR and FT-Raman spectra of **3** (Figures 4 and 5). The assignment of important vibrational frequencies of **3** is summarized in Table S4. The experimentally obtained $\nu(\text{Cr}\equiv\text{N})$ band at 1076 cm^{-1} matches well with the DFT-obtained $\nu(\text{Cr}\equiv\text{N})$ band at 1137 cm^{-1} with a scaling factor of 0.955. The obtained $\nu(\text{Cr}\equiv\text{N})$ vibrational frequency of **3** is observed at a slightly higher energy side in comparison with the earlier reported value of

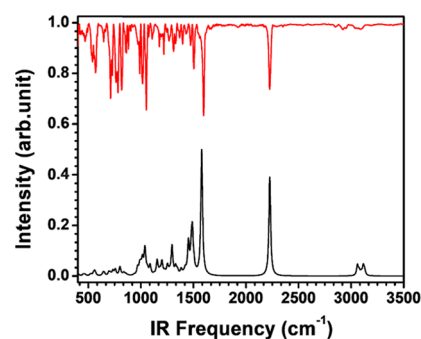


Figure 4. Experimentally obtained FT-IR spectrum of **3** (red line) and DFT computation-based IR spectrum of **3** (black line) (scaling factor of 0.955; Lorentzian broadening with an FWHM of $\sim 15\text{ cm}^{-1}$).

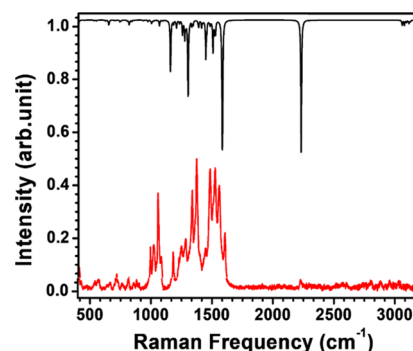


Figure 5. Experimentally obtained FT-Raman spectrum of **3** (red line) and DFT computation-based Raman spectrum of **3** (black line) (scaling factor of 0.955; Lorentzian broadening with an FWHM of $\sim 7\text{ cm}^{-1}$).

1017 cm^{-1} for a nitrido(porphyrinato)chromium(V) complex by Groves *et al.*^{38a} The $\nu(\text{Cr}\equiv\text{O})$ vibrational frequency of **1** is observed at 1064 cm^{-1} . Meanwhile, in both the complexes (**1** and **3**), most of the stretching vibrations are very much similar; however, the close comparison reveals that the vibration at 1076 cm^{-1} $\{\nu(\text{Cr}\equiv\text{N})\}$ is absent in the FT-IR spectra of the oxo(corrolato)chromium(V) complex. In analogy with that, the band at 1064 cm^{-1} $\{\nu(\text{Cr}\equiv\text{O})\}$ is also clearly missing in the FT-IR spectra of the nitrido(corrolato)chromium(V) complex. Meanwhile, comparing the FT-IR data of all the three complexes (**1**, **2**, and **3**), both the vibrations $\{\nu(\text{Cr}\equiv\text{O})$ and $\nu(\text{Cr}\equiv\text{N})\}$ are missing in the FT-IR spectra of **2**.

Electrochemistry. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were performed to understand the redox properties of complex **3**. The measurements are performed by using acetonitrile as a solvent and tetra-*n*-butyl ammonium perchlorate (0.1 M) as a supporting electrolyte (Table S1 and Figure 6). The Ag/AgCl reference electrode was also used to express potentials. The nitrido(corrolato)chromium(V) derivative, **3**, exhibited one reversible oxidation couple at $+0.53\text{ V}$ ($\Delta E_p = 80\text{ mV}$) vs Ag/AgCl. It also showed one reversible reduction couple at -0.06 V ($\Delta E_p = 80\text{ mV}$). These values are in good agreement with the values reported by Gross and Golubkov for a similar nitrido(corrolato)chromium(V) derivative.^{38b} This value is drastically different from that of an earlier reported nitrido(porphyrinato)chromium(V) derivative.³⁸ However, it is essentially very difficult to conclude the metal/ligand-centered redox processes from the electrochemistry data alone.

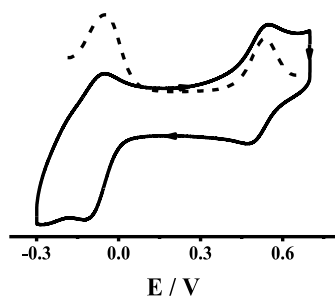


Figure 6. Cyclic (CV) (solid line) and differential pulse voltammogram (DPV) (dashed line) of [nitrido{5,10,15-tris(*p*-cyanophenyl)-corrolato}chromium(V)]⁻, **3**, in CH₃CN. The potentials are vs Ag/AgCl.

Spectroelectrochemical data are necessary to pinpoint the redox processes.

EPR Spectroscopy. The nitrido(corrolato)chromium(V) derivative, **3**, demonstrated EPR signals in solution at room temperature (Figure 7).

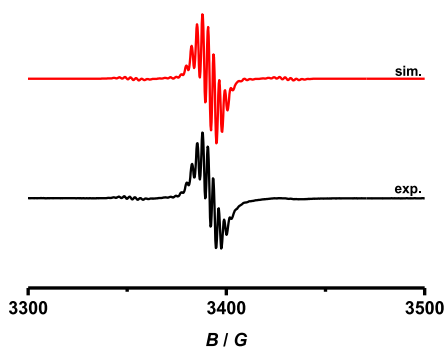


Figure 7. Experimental and simulated EPR spectrum of [nitrido-{5,10,15-tris(*p*-cyanophenyl)corrolato}chromium(V)]⁻, **3**, in CH₃CN at 298 K.

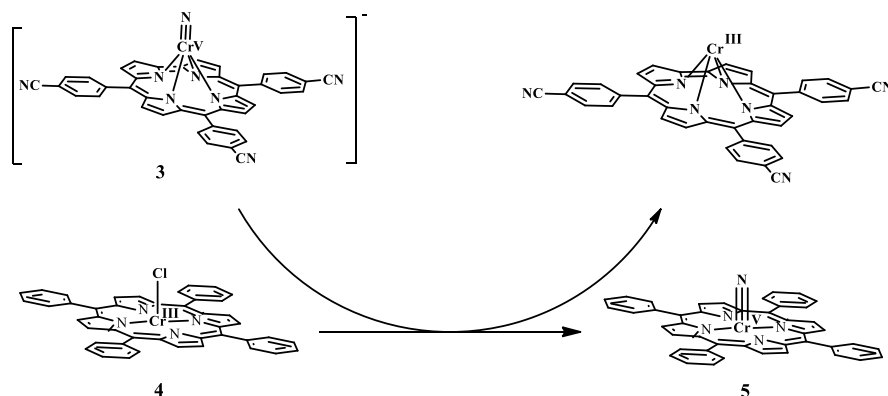
An isotropic EPR signal was obtained in fluid solution at RT. The spectrum of the nitrido(corrolato)chromium(V) derivative, **3**, shows 11 hyperfine lines. The origin of the 11 lines is due to the hyperfine coupling of the unpaired electron residing at the Cr center with the four pyrrolic nitrogen atoms and one nitrido nitrogen atom (99.6% ¹⁴N, *I* = 1). In addition to the 11 hyperfine lines, very weak satellite peaks are also present in the

spectrum. These peaks are due to the presence of a ⁵³Cr nucleus. This spectrum can be simulated by considering hyperfine coupling to five ¹⁴N (99.6% ¹⁴N, *I* = 1) nuclei and also to ⁵³Cr (*I* = 3/2, natural abundance of 9.5%; other isotopes, *I* = 0). The simulated EPR spectrum reproduced the experimental results with reasonable accuracy. Thus, in the native state, the oxidation state of chromium in compound **3** is also +5. The simulation of the EPR data of compound **3** provided the following parameters: *g*_{iso} = 1.987, *A*⁵³Cr = 26 G, and *A*¹⁴N = 2.71 G (Figure 7 and Table S2). These values are in line with the other earlier reported authentic nitrido(corrolato)chromium(V) and nitrido(porphyrinato)chromium(V) complexes.^{38a,b} The electronic configuration in the native state of compound **3** thus can be best described as [(cor³⁻)Cr^V(N³⁻)]⁻.

Nitrogen Atom Transfer Reactivity. The intermetal nitrogen atom transfer reaction was also studied between nitrido(corrolato)chromium(V), **3**, and a chloro(porphyrinato)chromium(III) complex, **4**. Although similar studies were described in a porphyrin framework,^{38d} it was never described earlier in a corrole metal complex. The progress of the nitrogen atom transfer reaction was studied by using a spectrophotometer. The kinetics of this reaction was studied by monitoring the change of absorption spectra of reactants and products as a function of time. The reaction between nitrido(corrolato)chromium(V), **3**, and a chloro(porphyrinato)chromium(III) complex, **4**, resulted in the formation of nitrido(porphyrinato)chromium(V), **5**, and a probable (corrolato)chromium(III) species (Scheme 3).

The reaction between nitrido(corrolato)chromium(V), **3**, and a chloro(porphyrinato)chromium(III) complex, **4**, in benzene solution is completed in 3–4 h, and the reaction is irreversible in nature. From the UV–Vis spectra of the end product, it is evident that this reaction resulted in the complete transfer of nitrogen atoms (Figure S10, see the Supporting Information). The end product of this reaction, i.e., the nitrido(porphyrinato)chromium(V) species, **5**, is fully characterized via UV–vis, IR, and EPR data (Figures S10–S12, see the Supporting Information). The end product (after complete transfer of nitrogen atoms) exhibited characteristic spectral data relevant to the presence of nitrido(porphyrinato)chromium(V) species,^{38g} **5**. A sharp Soret band at 421 nm and a Q band at 542 nm in benzene confirm the presence of compound **5** in the reaction mixture (Figure S10). The

Scheme 3. Schematic Representation of the Formation of Nitrido(porphyrinato)chromium(V), **5**, and a Probable (Corrolato)chromium(III) Species from the Precursor Complex Nitrido(corrolato)chromium(V), **3**, and a Chloro(porphyrinato)chromium(III) Complex, **4**



compound **5** (in the reaction mixture) also exhibited the $\nu(\text{Cr}\equiv\text{N})$ band at 1017 cm^{-1} , and it matches well with the literature-reported values (Figure S11).^{38g} An isotropic EPR signal was obtained in fluid solution at RT. The spectrum shows 11 hyperfine lines. The simulation of the EPR data of the end product provided the following parameters: $g_{\text{iso}} = 1.986$, $A^{53}\text{Cr} = 27.9\text{ G}$, and $A^{14}\text{N} = 2.96\text{ G}$ (Figure S12 and Table S2, see the Supporting Information).^{38g} The EPR data also suggest the presence of compound **5** in the reaction mixture. The kinetics of this reaction is measured for the change of absorbance as a function of time. A typical analysis is presented in the inset of Figure 8. A second-order rate constant

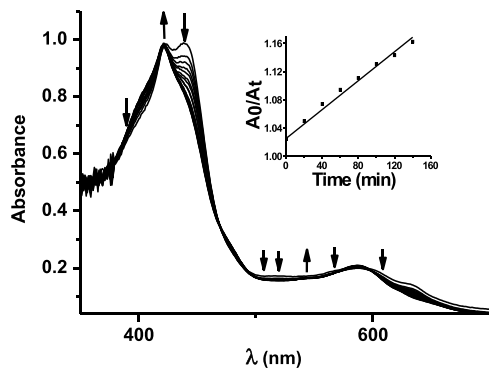


Figure 8. Time evolution of UV–Vis absorption spectra of an equal volume mixture of $0.4 \times 10^{-5}\text{ M}$ nitrido(corrolato)chromium(V), **3**, and $0.4 \times 10^{-5}\text{ M}$ (porphyrinato)chromium(III), **4**, in benzene in a cuvette (normalized). The inset shows the typical A_0/A_t vs time plot.

of $4.29 \pm 0.10\text{ M}^{-1}\text{ s}^{-1}$ is obtained. The rate constant for the reaction of nitridochromium(V) octaethylporphyrin and chlorochromium(III) tetraphenylporphyrins in benzene was reported to be 6.8 to $1420\text{ M}^{-1}\text{ s}^{-1}$.^{38d} A mechanism has been proposed by Bottomley and Neely for these kinds of intermetal N atom transfer reactions. We also believe that a similar type of mechanism is also involved here. A μ -nitrido intermediate is generated *via* the nucleophilic attack of nitrogen atoms of nitrido(corrolato)chromium(V) to the backside of chloro-(porphyrinato)chromium(III).^{38e} Although there is no direct proof available for the existence of μ -nitrido intermediate species in solution, keeping the reaction mixture at a higher temperature for several hours also does not lead to any back reaction. It thus supports that the driving force of this nitrogen atom transfer reaction is purely thermodynamic in nature.^{38e}

Additionally, the energetics of the intermetal nitrogen atom transfer reaction was also studied by employing DFT calculations. All the reactants {nitrido(corrolato)chromium(V), **3**, and the chloro(porphyrinato)chromium(III) complex, **4**} and products {nitrido(porphyrinato)chromium(V), **5**, and (corrolato)chromium(III) species} were optimized at the B97D level of theory. The free energy values were calculated by using the SMD solvation model by performing a single-point energy calculation in a benzene solvent. Zero-point energy correction was done while calculating the free energies of the product formation. The schematic presentation of the nitrogen atom transfer reaction and the energetics of reactants and products are depicted in Figure S13. The higher product energy ($\Delta G = 36.7\text{ kcal/mol}$) with respect to the reactants indicates the endothermic nature of the reaction. The involvement of multiple transition states and intermediates in the reaction mechanism has been ignored in the energy profile

diagram. However, we could optimize one possible reaction intermediate, i.e., (corrolato)chromium(V)-nitrido-chromium(III) (porphyrinato) (Figure 9). This species is probably

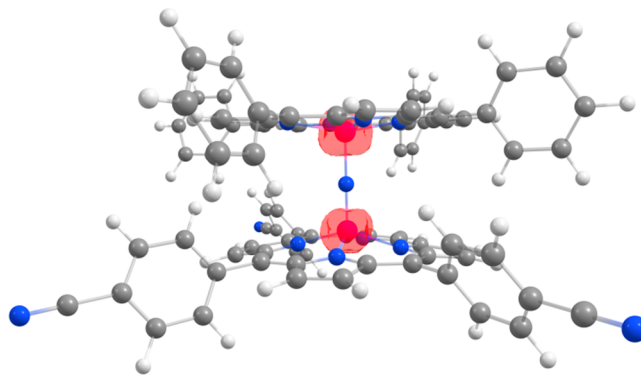


Figure 9. Spin density representations for the μ -nitrido intermediate complex: (corrolato)chromium(V)-nitrido-chromium(III) (porphyrinato) (iso-value of 0.02). The quintet ground state was used for computation.

involved in the N atom transfer reaction from the nitrido-(corrolato)chromium(V) moiety to the (porphyrinato)-chromium(III) moiety with concomitant electron transfer. It is worthwhile mentioning here that we have optimized the energy profile of the reactants and products, and based on that, we have calculated the corresponding free energy change. Thus, a direct correlation between the asymmetric nitride-bridged intermediate complex (Figure 9) with the computed thermodynamics is not possible.

It has been shown experimentally that the intermolecular interaction in the $\cdots\text{Cr}-\text{N}\equiv\text{Cr}-\text{N}\cdots$ chain structure (in a polymeric nitridochromium(V) complex) is ferromagnetic in nature.^{37g} In the proposed reaction intermediate, i.e., (corrolato)chromium(V)-nitrido-chromium(III) (porphyrinato), the Cr(V) is inside the corrole ring and has a coordination number of 5 and has one unpaired electron, and the Cr(III) inside the porphyrin cavity has also a coordination number of 5 and has three unpaired electrons. In analogy with the earlier observations,^{37g} we have assumed that the reaction intermediate has an $S = 2$ ground spin state. From the DFT-optimized structure, it is clearly evident that the Cr–N bond distance (1.64 \AA) of the (corrolato)chromium section of the μ -nitrido dimer is relatively longer than that of the Cr–N bond distance (1.53 \AA) of the (corrolato)chromium(V) nitrido complex. This clearly explains the strong affinity of nitrogen atoms toward the (porphyrinato)chromium(III) moiety. Thus, the structural analysis of this most probable intermediate species clearly explains the observed N atom transfer reactivity. The spin density representation of the μ -nitrido intermediate complex is shown in Figure 9. The calculated spin density on chromium in the (corrolato)chromium(V) section of the dimer is 2.76 and in the (porphyrinato)chromium(III) section is 2.55. Thus, a significant intermetal spin density transfer occurs in the μ -nitrido intermediate complex.

CONCLUSIONS

In conclusion, a new nitrido(corrolato)chromium(V) complex has been synthesized. The precursor complex, oxo(corrolato)-chromium(V), has been successfully transformed into the corresponding nitrido(corrolato)chromium(V) complex by using a nitrido group transfer reagent. The most widely used

synthetic strategy for nitrido chromium(V) complexes involves the N atom transfer from Mn^V(N)(salen/salophen) to a Cr(III) derivative. However, we have transferred the nitrogen atom directly from Mn^V(N)(salophen) to an oxo(corrolato)chromium(V) derivative *via in situ* reduction by using a PPh₃ ligand. DFT calculations were also performed on the nitrido(corrolato)chromium(V) complex in addition to the spectroscopic characterizations. Our studies confirm that complex **3** has a paramagnetic d¹ electronic configuration. The experimentally obtained EPR spectrum can be simulated with reasonable accuracy by considering hyperfine coupling to five ¹⁴N nuclei and also to ⁵³Cr. The simulation of the EPR data of compound **3** provided the following parameters: $g_{\text{iso}} = 1.987$, $A^{53}\text{Cr} = 26$ G, and $A^{14}\text{N} = 2.71$ G. The nitrido(corrolato)chromium(V) derivative, **3**, exhibited one reversible oxidation couple at +0.53 V. It also showed one reversible reduction couple at -0.06 V *vs* Ag/AgCl. These redox potential values are drastically different compared to the related nitrido(porphyrinato)chromium(V) derivatives.^{38b} Compound **3** exhibited a sharp Soret band at 438 nm and a Q band at 608 nm. The absorbance maxima at 438 and 608 nm are thus assigned as ILCT transitions. The chromium–nitrogen (nitrido) bond distance obtained in the DFT-optimized structure of **3** is 1.530 Å. This short chromium–nitrogen (nitrido) bond distance indicates triple bond formation between chromium and nitrogen. Thus, a combination of nitride and corrole ligand functionalities would be perfect for stabilizing higher oxidation states of chromium. Reactions of nitrido(corrolato)chromium(V), **3**, with the chloro(porphyrinato)chromium(III) complex, **4**, resulted in the formation of nitrido(porphyrinato)chromium(V), **5**, and a probable (corrolato)chromium(III) species. A second-order rate constant of $4.29 \pm 0.10 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for this complete intermetal N atom transfer reaction between chromium(V) corrole and chromium(III) porphyrin complexes. A bimetallic μ -nitride intermediate is the probable intermediate for this reaction, and a net two-electron transfer occurs. Work is in progress to find suitable nitrido(corrolato)chromium(V) derivatives that will transfer nitrogen atoms to different organic substrates.

EXPERIMENTAL SECTION

Materials. Pyrrole, chloranil, Cr(CO)₆, and TBAP (tetrabutylammonium perchlorate) were purchased from Sigma-Aldrich (USA). *p*-Cyanobenzaldehyde was purchased from Merck (India). Hexane and dichloromethane were obtained *via* distillation from KOH and CaH₂, respectively. The rest of the starting chemicals were of reagent grade. Oxo-[5,10,15-tris(*p*-cyanophenyl)corrolato]chromium(V), **1**, was synthesized by following a literature-reported method.³⁹ (Saloph)Mn^V(N) was prepared by following a literature-reported method.⁴¹ 5,10,15-Tris(4-cyanophenyl)corrole was prepared according to a literature-reported protocol.²⁴ The chloro(porphyrinato)chromium(III) complex, **4**, was also prepared by following a literature-reported method.^{38f}

Physical Measurements. The C/H/N analysis was performed with a Euro EA elemental analyzer. A PerkinElmer spectrophotometer (LAMBDA-750) was used to record the UV–Vis spectra. A PerkinElmer spectrophotometer was used to record FT-IR spectra. The samples were prepared as KBr pellets. A LabRAM HR Evolution (Horiba Scientific) was used to record the Raman spectra. A Bruker AVANCE 400 MHz NMR spectrometer was used to record the NMR data.

Tetramethylsilane (TMS) was the internal standard. A Bruker Micro TOF-QII mass spectrometer was used to record the electrospray mass spectra (ESI-MS). An electrochemical instrument (CS 350, China) was used to record the cyclic voltammetric measurements. A platinum wire (as an auxiliary electrode), glassy carbon (as a working electrode), and Ag/AgCl (as a reference electrode) were used in a traditional three-electrode cell. TBAP (tetrabutylammonium perchlorate, 10⁻¹ M) was used as the supporting electrolyte. The concentration of the complex solution was mentioned to be 10⁻³ M. The E_{298}^0 (half-wave potential) was set equal to 0.5 ($E_{\text{pa}} + E_{\text{pc}}$) { E_{pa} = anodic peak potentials and E_{pc} = cathodic peak potentials}. The scan rate was 100 mV s⁻¹. EPR spectra were recorded with a Bruker EMX System (ER 073) (X-band frequency of ca. 9.5 GHz). Synthetic quartz glass tubes were used for the measurements.

Computational Methods. Ground-state geometry optimization of the studied complexes was performed by density functional theory (DFT). The B97 functional was used with dispersion correction (B97D) as implemented in the Gaussian 16 program.^{42,43} The B97D functional provides reliable spectroscopic parameters that reasonably match the experimental data.⁴⁴ For hydrogen, carbon, and nitrogen, the 6-31G(d) basis set was used. The TZVP basis set was used for chromium. An IEF-PCM solvent model was implemented in the calculation considering acetonitrile as the solvent. The vibrational frequency calculations were also performed at the same level of theory to ensure that the optimized structure was at the true minima. The same functional and basis sets were used for the time-dependent DFT calculations (TD-DFT). The free energy values were calculated by using the SMD solvation model by performing a single-point energy calculation on the gas-phase optimized geometries in a benzene solvent. Zero-point energy correction was done while calculating the free energies of the product formation.

Synthesis of Oxo[5,10,15-tris(*p*-cyanophenyl)corrolato]chromium(V),³⁹ **1.** 5,10,15-Tris(*p*-cyanophenyl)corrole²⁴ (48 mg, 0.081 mmol) was dissolved in 24 mL of toluene. Excess Cr(CO)₆ was added to the reaction vessel. Reflux with stirring was continued for 2–3 h. The color of the solution gradually changed to deep red. The solution was cooled to room temperature, and the unreacted Cr(CO)₆ crystals were removed. The solvent was evaporated to dryness by using a rotary evaporator, and the product was purified by silica gel column chromatography (100–200 mesh, CH₂Cl₂/hexane). Recrystallization yielded a deep red crystalline solid. Yield: 48% (25 mg, 0.0375 mmol). Anal. calcd for C₄₀H₂₀CrN₇O (**1**): C, 72.07; H, 3.02; N, 14.71. Found: C, 72.15; H, 2.97; N, 14.61. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) in acetonitrile: 404 (86000), 557 (15500) (Figure S1). HRMS (ESI-TOF) m/z : [M]⁻ calcd for C₄₀H₂₀CrN₇O, 666.1130; found, 666.1124 (Figure S3). All the values matched nicely with the earlier reported values.³⁹

Synthesis of {Bis(triphenylphosphineoxide)}[5,10,15-tris(*p*-cyanophenyl)corrolato]chromium(III), **2.** **1** (26 mg, 0.039 mmol) was dissolved in 10 mL of a CH₂Cl₂ + CH₃CN mixture (9:1) under a N₂ atmosphere. Then, excess PPh₃ was added to it under stirring conditions. The reaction mixture was stirred continuously for 5 min during which the color of the reaction mixture changed from red to greenish-red. As this compound is highly air-sensitive, thus, it is not possible to purify it *via* column chromatography. This crude reaction mixture was used for further characterization of this

compound. $\lambda_{\text{max}}/\text{nm}$ in the $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$ (9:1) mixture (with PPh_3 and OPPh_3): 445, 602, 643, 708 (Figure S6). MS (ESI-TOF) m/z : $[\text{M} + \text{OH}]^+$ calcd for $\text{C}_{76}\text{H}_{51}\text{CrN}_7\text{O}_3\text{P}_2$, 1223.2934; found, 1223.4494 (Figure S5). EPR X-band, 100 K, $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$ (9:1) mixture: $g_{\text{av}} \approx 1.982$ (Figure S8).

Synthesis of [Nitrido{5,10,15-tris(*p*-cyanophenyl)-corrolato}chromium(V)]⁻ [(Saloph)Mn^{III}]⁺; 3, [(Saloph)-Mn^{III}]⁺. **1** (26 mg, 0.039 mmol) was dissolved in 10 mL of a $\text{CH}_2\text{Cl}_2 + \text{CH}_3\text{CN}$ mixture (9:1) under a N_2 atmosphere. Then, 18 mg (0.047 mmol) of solid (saloph)Mn^V(N) and excess PPh_3 were added to it under stirring conditions. The reaction mixture was stirred continuously for 5 min during which the color of the reaction mixture changed from red to green. Then, the reaction was stopped, and the solvent was evaporated by a rotary evaporator. The crude mixture was washed 6–7 times with a DCM:hexane (1:1) mixture to remove excess PPh_3 and OPPh_3 . After that, the compound was purified through a silica column (CH_3CN), and the desired compound was collected (purple solid). Yield: 62% (16 mg, 0.024 mmol). $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) in acetonitrile: 438 (134,500), 506 (9600), 540 (12,500), 608 (35,900). HRMS (ESI-TOF) m/z : $[\text{M}]^-$ calcd for $\text{C}_{40}\text{H}_{20}\text{CrN}_8$, 664.1211; found, 664.1216 (Figure S4).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c02267>.

UV–Vis, FT-IR, EPR, and ESI-MS data of **1** and **2**; UV–Vis, FT-IR, electrochemical, EPR, ESI-MS, and TD-DFT data of **3** and selected molecular orbitals of **3**; UV–Vis, FT-IR, and EPR data of the reaction mixture of nitrido(corrolato)chromium(V), **3**, and (porphyrinato)-chromium(III), **4**, in benzene; optimized Cartesian coordinates of the reactants, products, and intermediates (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

DAE (Department of Atomic Energy)-India is gratefully acknowledged for funding. We would like to acknowledge NISER-Bhubaneswar for providing infrastructure facilities. Financial support provided by the SERB (Science & Engineering Research Board; EMR/2016/005484)-India is gratefully acknowledged.

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