High-Oxidation-State Cr Complexes

Chromium(v) and Chromium(vi) Nitrido Complexes of Tris(pentafluorophenyl)corrole**

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A unique feature of corroles relative to porphyrins and other related ligands is their ability to stabilize transition-metal ions in high oxidation states.^[1,2] This phenomenon can not be related to the traditional means of obtaining high-valent metal complexes, which relies on π -donating and nonoxidizable ligands such as $F^{-},\ O^{2-},$ and $N^{3-},$ since the corrole macrocycle in non-transition-metal complexes is easily oxidized.^[3] Instead, recent theoretical and experimental evidence suggests that σ donation by corrole trianions raises the energy of metal d orbitals to a large extent. This leads to destabilization of low-valent oxidation states and is also manifested in the unique activation of molecular oxygen by chromium(III) and iron(III) corroles.^[4,5] Taken together, the cooperation of both π and σ effects in oxo- and nitridometallocorroles could be an attractive methodology for obtaining novel complexes. The validity of this hypothesis is indicated by the stability of corrole complexes with pentavalent metal ions: $[(tpfc)Cr^{V}(O)] (1)$, [4b] $[(tpfc)Mn^{V}(O)] (2)$,[6] $[(tpfc)Mn^{V}(N)]^{-}$ (3),^[7] and $[(tpfc)Mn^{V}(NAr)]$ (4),^[8] where tpfc stands for the trianion of 5,10,15-tris(pentafluorophenyl)corrole (Scheme 1).^[9] However, complexes of the highly oxidizing Cr^{VI} ion were not reported for corroles or other related ligands.^[10] A relevant result that explains why such complexes could not be obtained is that the one-electron oxidation of 1 is corrole- rather than metal-centered and leads to $[(tpfc)Cr^{V}(O)]^{+}$ rather than $[(tpfc)Cr^{VI}(O)]^{+}$.^[11] Since a comparison of nitrido and oxo complexes with identical ligands and metals reveals that the former are invariably more stable, we decided to explore the possibility of obtaining stable (nitrido)chromium corroles. These attempts were successful: both $[(tpfc)Cr^{V}(N)]^{-}$ (5a) and $[(tpfc)Cr^{VI}(N)]$ (5b) were isolated and characterized by a combination of spectroscopic methods and electrochemistry.

The first approach was to treat $[(tpfc)Cr^{III}(py)_2]$ (6) with an excess of NH₃ in the presence of a mild oxidant, under the assumption that ligand substitution and subsequent oxidation of the coordinated ammonia would lead to an imido or nitrido complex. Using Br₂ or *N*-bromosuccinimide (NBS), the reaction proceeded to the Cr^V(N) state, but partial bromination (up to four) of the β -pyrrolic C–H bonds of the corrole took place concurrently. On the other hand, the oxo complex

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Scheme 1. Formulas of recently reported oxo-, imido-, and nitridometallocorroles and of the new chromium complexes.

1 was formed when iodosylbenzene was utilized as oxidant. Because of these limitations, a very different route was adopted. It consists of preparing the stable (nitrido)manganese(v) complex of salophene,^[12] [(saloph)Mn(N)] (**7**), and transferring its nitrogen atom to **6** (Scheme 2).^[13]



Scheme 2. Synthesis of $[(tpfc)Cr^{V}(N)]^{-}$ (**5** a) by nitrogen-atom transfer from [(salop)Mn(N)] (**7**) to $[(tpfc)Cr^{III}(pyr)_2]$ (**6**).

Pronounced changes occur when the two reagents are mixed: Compund **6** is green and displays a very rich electronic spectrum, while **5a** is purple-green and shows a sharp Soret band at 427 nm and a characteristic Q band at 585 nm (Figure 1). Similar to the previously reported (nitrido)manganese(v) complex **3**, **5a** is particularly stable in acetonitrile, and accordingly the spectroscopic measurements were performed in this solvent. The strongest support for the assignment of **5a** as a (nitrido)chromium(v) complex resulting from a two-electron atom transfer from **7** is provided by EPR



Figure 1. Spectral changes upon transformation of $[(tpfc)Cr^{|||}(pyr)_2]$ (6) into $[(tpfc)Cr^{\vee}(N)]^-$ (5 a) by addition of [(salop)Mn(N)] (7).

spectroscopy. The spectrum of **5a** (Figure 2b) is similar to that of the (oxo)chromium(v) complex **1** (Figure 2a): both display hyperfine coupling to ⁵³Cr ($A_{^{53}Cr}$) and superhyperfine coupling to nitrogen atoms ($A_{^{14}N}$) at room temperature. The presence of five ¹⁴N atoms in **5a** as opposed to four in **1** is clearly evident from the 11 rather than nine lines, best seen in the inset of Figure 2b. In addition, the $A_{^{53}Cr}$ value of 2.67 mT in **5a** is within the range of 2.49–2.84 mT obtained for other (nitrido)chromium(v) complexes and, as expected, much larger than in **1** (1.96 in CH₃CN and 1.64 mT in CH₂Cl₂).



Figure 2. EPR spectra (in CH₃CN at RT) of a) [(tpfc)Cr^V(O)] (1), b) [(tpfc)Cr^V(N)]⁻ (**5** a), c) [(¹⁵N₄-tpfc)Cr^V(N)]⁻ (¹⁵N₄-**5** a), and d) [(tpfc)Cr^V(¹⁵N)]⁻ (**5** a⁻¹⁵N). Insets: experimental (exp) and simulated (sim) spectra of the low-field region.

Examination of Figure 2b reveals one A_{14N} value of about 0.27 mT for all five nitrogen atoms. This is reminiscent of the recurring puzzle in the EPR spectra of all (nitrido)chromium(v) complexes with equatorial N donors (for example, salen, cyclam, and porphyrins),^[14] in which the isotropic hyperfine couplings to the axial nitrido ligand and the other nitrogen atoms were found to be practically identical, with $A_{14N} = 0.23 - 0.28$ mT. What is more, A_{14N} (nitrido) = 0.29 mT in the pentacyano(nitrido)chromium(v) complex prepared by Jesper et al.,^[15] the only example to date for which the superhyperfine coupling tensor to a nitrido ligand could be measured independently of couplings to other nitrogen atoms. In an attempt to solve the puzzle, analogues of 5a in which either the four nitrogen atoms of the corrole or the unique nitrido ligand are ¹⁵N-labeled ($[(^{15}N_4-tpfc)Cr^V(N)]^-$ (¹⁵N₄-5a) and $[(tpfc)Cr^{V}(^{15}N)]^{-}$ (5a-¹⁵N), respectively) were prepared.^[16] The spectra shown in Figure 2c and d reveal significantly different superhyperfine coupling constants, and the best simulations were achieved with A_{14N} (nitrido) = 0.26 mT and A_{14N} (corrole) = 0.36 mT for ¹⁵N₄-5a and A_{14N} (nitrido) = 0.36 mT and A_{14N} (corrole) = 0.27 mT for **5 a-**¹⁵N. Since the isotropic hyperfine coupling constant of ¹⁵N is 40% larger than that of ¹⁴N,^[17] these measurements prove that the hyperfine couplings to the axial nitrido ligand and the other nitrogen atoms in complex 5a are indeed identical.

Another major difference between 5a and 1 is found in their cyclovoltammograms (Figure 3). As expected, nitrido complex 5a is harder to reduce and easier to oxidize than oxo



Figure 3. Cyclovoltammograms (in CH₃CN at RT) of a) [(tpfc)Cr^V(O)] (1) and b) [(tpfc)Cr^V(N)]⁻ (5 a).

complex **1**. Furthermore, the difference between the corresponding $E_{1/2}$ values in **5a** is only 0.59 V, and both its reduction and oxidation potentials (-0.03 and +0.56 V, respectively) are far from the values required for corrole-centered redox processes (< -1 and > +1 V, respectively).^[3b] This is remarkably different from the (nitrido)chromium(v) porphyrin [(tpp)Cr(N)],^[14a] whose redox potentials of -1.08

and +1.04 V are supportive of porphyrin- rather than chromium-centered processes.

Since the electrochemistry of **5a** suggested that the (nitrido)chromium(vI) complex **5b** should be quite stable, the chromium(III) complex **6** was treated with sodium hypochlorite.^[18] In contrast to porphyrin and salen complexes, for which this is the method of choice for preparation of the corresponding (nitrido)chromium(v) complexes,^[12,14] the sole reaction product in the case of **6** was **5b** and not **5a**. This was proven by spectroscopy: **5b** is EPR-silent and displays well-resolved ¹⁹F and ¹H NMR spectra (Figure 4). This is perfectly in line with expectations for a genuine chromium(vI) complex (d⁰).^[19]



Figure 4. 1H (inset) and ^{19}F NMR spectra of [(tpfc)Cr $^{VI}(N)$], 5b, in CD_3CN at RT.

This study shows that the combination of σ donation by corrole trianions and π donation by N^{3-} is a fruitful approach for the preparation of metal complexes with unusually high oxidation states. The (nitrido)chromium(v) corrole was prepared by nitrogen-atom transfer from (nitrido)manganese(v) salophene, which also serves to demonstrate the large thermodynamic stability of the former complex. The ammonia/sodium hypochlorite method that is extensively used for the preparation of (nitrido)chromium(v) complexes of porphyrins and salens leads to (nitrido)chromium(vi) when applied to chromium(III) corroles.

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- [13] [(tpfc)Cr^V(N)]⁻ (**5a**): Solid [(saloph)Mn^V(N)] (22 mg, 57.4 µmol) was added to a solution of [(tpfc)Cr^{III}(py)₂] (25 mg, 29.6 µmol) in acetonitrile (10 mL). After the color change from green to purple was complete (1 min, also monitored by UV/Vis), **5a** (16 mg, 18.6 µmol) was isolated by column chromatography (silica gel, CH₃CN). MS⁻: m/z (%): 859 [M^-] (100), 845 [M^- –N], 80 %; UV/Vis (CH₃CN) λ_{max} (relative ε): 427 (100), 585 nm (15); ¹⁹F NMR (188 MHz, CD₃CN): δ = –139.0 (brs, 6F), –156.6 (brs, 3F), –163.6 ppm (brd, 6F).
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- [16] 15 N₄-5**a**: The labeled corrole was prepared by solvent-free condensation of [15 N]pyrrole (Aldrich) and pentafluorobenzaldehyde.^[8] Insertion of chromium(III) ions and atom transfer from [(saloph)Mn^V(N)] (13.5 mg, 35.3 µmol) to [(15 N₄-tpfc)Cr^{III}(py)₂] (15 mg, 17.7 µmol) in acetonitrile (5 mL) provided 15 N₄-5**a** (14 mg, 16.2µmol). MS⁻: m/z (%): 863 [M^{-}] (45), 849 [M^{-} - 14 N]. 5**a**- 15 N: [(saloph)Mn^V({}^{15}N)] (27.7 mg, 72 µmol) was prepared by addition of 15 NH₄OH (3 N, 0.68 mL, 2 nmol) and sodium hypochlorite (7 mL, 0.28 mmol) to [(saloph)Mn^{III}Cl] (50 mg, 135 µmol) in methanol (5 mL). Atom transfer from [(saloph)Mn(15 N)] (8.2 mg, 21.3 µmol) to [(tpfc)Cr^{III}(py)₂] (15 mg, 17.8 µmol) in acetonitrile (5 mL) yielded 5**a**- 15 NI (14 mg, 16.3 µmol). MS⁻: m/z (%): 860 [M^{-}] (50), 845 [M- 15 NI (100%).
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- [18] [(tpfc)Cr^{VI}(N)], **5b**: Pyridine (1 drop), NH₄OH (0.014 mL, 0.36 mmol), and sodium hypochlorite (7.5 mL, 0.14 mmol) were added to a solution of $(tpfc)Cr^{III}(py)_2$ (25 mg, 24.9 µmol) in acetonitrile (10 mL) under argon. After the color change from green to purple was complete (1 min, also monitored by UV/

Vis), sodium sulfate was added, and the solution was filtered and evaporated to dryness to afford **5b** (21.3 mg, 24.8 µmol). MS⁻: m/z (%): 859 [M^{-}] (10); UV/Vis (MeOH) λ_{max} (relative ε): 429 (100), 581 nm (25); ¹ H NMR (200 MHz, CD₃CN): δ = 9.32 (d, J = 3.99 Hz, 2H), 8.97 (d, J = 3.81 Hz, 2H), 8.93 (d, J = 4.54 Hz, 2H), 8.79 ppm (d, J = 4.34 Hz 2H); ¹⁹F NMR (188 MHz, CD₃CN): δ = -138.8 (d, J = 23.9 Hz, 2F), -138.9 (d, J = 20.7 Hz, 1F), -139.5 (d, J = 24.05 Hz, 2F), -139.6 (d, J = 28.7 Hz, 1F), -156.6 (t, J = 20.4 Hz, 2F), -156.8 (t, J = 20.2 Hz, 1F), -164.0 ppm (m, 6F).

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