Inorganic Chemistry
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Metallocorrole Dendrimers: Sensitive Corrole–Chromium(V)–Nitride Spin Probes for Studying the Solution Structure of Dendrimers

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S *Supporting Information*

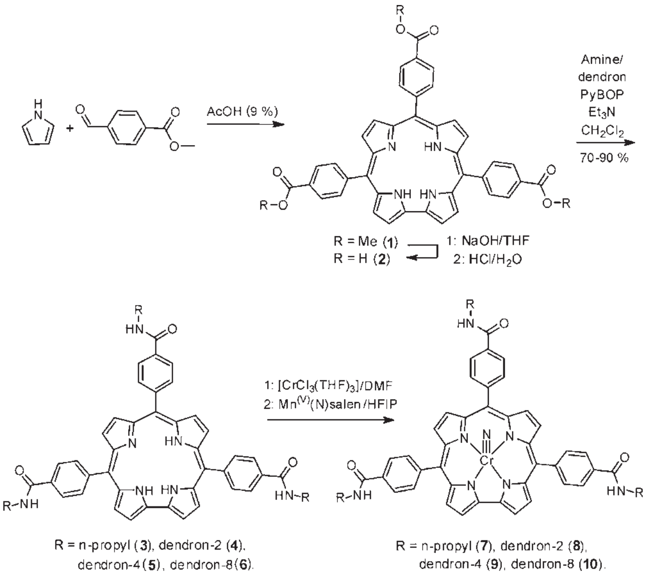
ABSTRACT: The corrole–chromium(V)–nitrido moiety is introduced as a uniquely sensitive EPR spin probe. We describe a series of corrole-centered poly(amidoamine) (PAMAM) dendrimers and the selective incorporation of the chromium(V)–nitrido moiety. The chromium–corrole cores are reactive toward both neutral and charged reagents, and the accessibility of the dendrimer cores enables easy manipulation of the spin probe. The spin probe reveals a pronounced solvent dependence of the solution-phase structure of the dendrimers.

The three-dimensional structure of dendrimers makes them promising models for biological macromolecules such as enzymes and proteins.[1] The use of dendrimers as models for biological systems encourages investigations into their structure in solution,[4] and the design, synthesis, and characterization of new dendrimers incorporating functionalities capable of reporting subtle changes in the environment present an important challenge.[2–6] Electron paramagnetic resonance (EPR) spin probes have been used extensively in the study of biomacromolecule structure and dynamics.[7] EPR spin probes have been applied to investigate the structures of dendrimers using various organic radicals, but the incorporation of a sensitive spin probe at the center of dendrimers would enable a direct study of their solution phase properties.[8]

In recent work, we showed that the chromium(V)–nitrido unit can function as a uniquely sensitive spectroscopic spin probe for reactivity toward electrophiles.[9] Here we demonstrate how corroles can be used as a highly selective site for the preparation of chromium(V) nitrides. We incorporate chromium(V) nitrides inside large poly(amidoamine) (PAMAM) dendrimers and show how this can be used to probe the solution-phase behavior of the dendrimer. Metallocorroles[10] have received attention as catalysts for epoxidation,[11] atom transfer,[12] water oxidation,[13] and aziridination.[14]

A series of corrole-centered PAMAM dendrimers was synthesized following a convergent synthesis approach similar to our previously reported syntheses of PAMAM dendrimers (Scheme 1); a triphenylcorrole functionalized with three carboxylic acids was utilized as the core of the dendrimer.[15] The corrole trimethylester (**1**) was conveniently prepared according to the procedure of Paolesse and co-workers, with some modifications in the purification procedure, enabling routine isolation of 2 g batches. The triacid (**2**) was obtained by means of basic hydrolysis of the triester.[16] *tert*-Butyloxycarbonyl deprotection of the dendrons (25% trifluoroacetic acid in CH_2Cl_2) and amide bond formation via coupling with PyBOP gave the dendrimers **4**–**6** and the model tripropylamide **3**. The resulting dendrimers **4**–**6** possess a corrole core, a PAMAM-type interior, and benzyl esters at the periphery (Figure 1).

Scheme 1. Synthesis of Corrole-Centered PAMAM Dendrimers and Metal Insertion Protocol, Followed by Nitrogen Atom Transfer To Give the Chromium(V)–Nitrido Complexes



The corroles were converted into the corresponding chromium(III) complexes by reaction with labile $[CrCl_3(THF)_3]$ (THF = tetrahydrofuran) in *N*,*N*-dimethylformamide (DMF) in a microwave reactor. It should be noted that failure to strictly observe anaerobic conditions led to the formation of chromium(V)–oxo species, clearly demonstrating the preference for high oxidation states in corrole chemistry, as shown in the work of Gross et al.[17] The chromium(III) complexes were transformed into the corresponding chromium(V)–nitrido complexes by treatment with $Mn^V(N)$salen in DMF/hexafluoroisopropyl alcohol.[18] This type of nitrogen atom transfer has been investigated mechanistically by Groves and Takahashi,[19a] Neely and Bottemley,[19b] Woo and Goll,[19c] and Gray et al.[19d] Notably, the reaction has been shown unambiguously to be inner-sphere,[19b] requiring a nitride-bridged intermediate, and to be reversible.[19d]

Received: April 11, 2011
Published: June 02, 2011

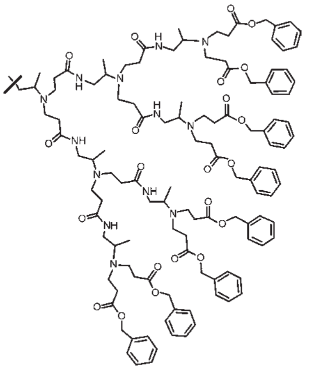


Figure 1. Structure of the PAMAM dendron arms exemplified by dendron-8 of compound **6**.

The resulting chromium(V)−nitrido complexes and dendrimers (**7** and **8**−**10**, respectively) were isolated using preparative-scale size-exclusion chromatography in CH_2Cl_2. All corrole-centered dendrimers were analyzed by UV/vis spectroscopy and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. In addition, the metal-free systems were characterized by NMR spectroscopy and the metalated systems by EPR spectroscopy.

The chromium(V)−nitrido-functionalized dendrimers (**8**−**10**) show insignificant variation in the Soret band energies with the dendrimer size. However, contrary to the uncomplexed corrole dendrimers, the bandwidths are constant across the three generations (Supporting Information). It is noteworthy that all of the corrole amides exhibit significant photostability in solution, as demonstrated by following the change in absorbance of the Soret band over time upon leaving solutions of the corroles under ambient laboratory light and ambient atmosphere. We note that the addition of only one carboxy substituent per *meso*-phenyl substituent is sufficient to achieve this photostability.[20]

As d^1 systems, chromium(V)−nitrido complexes generally yield fairly narrow solution-phase EPR spectra with $g \approx 2$.[21] Furthermore, superhyperfine coupling of the electron spin to the nuclear spins of the ligating nitrogen donors is expected to yield a splitting of the signal. If the superhyperfine coupling is near identical for all of the ligating nitrogen atoms, as is frequently found experimentally,[19] the splitting will result in $2I_{\text{tot}} + 1 = 11$ equidistant lines for five equivalently coupled nitrogen donors [$I(^{14}N) = 1$], as in the chromium(V)−nitrido-functionalized corroles. Weak satellites from coupling to ^{53}Cr (9.5%, $I = {}^{3}/_{2}$) are detectable for small molecules.[22] Solution-phase EPR spectra of the simple chromium(V)−nitrido-functionalized corrole ester (**1**) and amide (**3**) as well as of the chromium(V)−oxo corrole ester (**11**), which forms by air oxidation of the chromium(III) complex, exhibit a resonance with $g \approx 1.98$ split into the expected number of lines (11, 11, and 9, respectively) by superhyperfine couplings to ligating nitrogen atoms (Supporting Information). The coupling constants fall within 10% of those observed for related chromium(V) complexes.[3,22]

In recent work, we found that functionalization of chromium(V)−nitrido complexes, either by conversion to imides or by nitrido bridge formation to low-valent platinum metal ions, results in dramatic, counterintuitive, increases in superhyperfine couplings.[9] This result also applies to the chromium(V)−nitrido-complexed corrole ester (**1**), when compared to the tritylated species Cr^{V}(N-trt), as shown in Figure 2b, illustrating the increase in complexity and splitting of the spectrum over that of the simple nitride precursor (Figure 2a). The value of $A(^{14}N_{\text{axial}})$ approximately doubles upon functionalization. Similar increases in the nitrogen superhyperfine coupling were found for nitrido-bridged complexes formed by reaction with $[Pt(C_2H_4)Cl_3]^-$ or $[Rh(COD)Cl]_2$; the tripropylamide-substituted corrole (**3**) behaved analogously (Supporting Information).

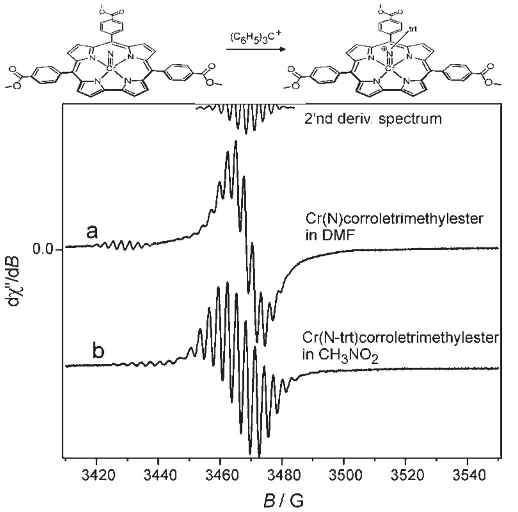


Figure 2. Top: Nitride functionalization with trityl. Bottom: EPR spectra of (a) corrole triester **1** coordinating Cr^{V}(N) and (b) Cr^{V}(N-trt) [trt = $C(C_6H_5)_3$]. The top trace is the derivative of trace (a) which facilitates the counting of the 11 superhyperfine components.

In the EPR spectra of the chromium(V)−nitrido dendrimers, on the other hand, only very poorly structured bands around $g = 2$ without resolved superhyperfine couplings were observed (Figure 3a−c). The lacking resolution of the superhyperfine couplings for the dendrimers can be attributed to a combination of additional spin−spin interactions from the hydrogen atoms of the dendron arms and incomplete averaging of the anisotropic couplings due to intermediate tumbling rates on the EPR time scale. Importantly, also for the dendrimers, the reaction with $C(C_6H_5)_3^+$ resulted in a large increase in the superhyperfine coupling and a concomitant marked increase in the resolution of the dendrimer EPR spectra, as illustrated in Figure 3d−f. The effect is similar for all three generations of dendrimers. Attempts to react the dendrimers with $[Pt(C_2H_4)Cl_3]^-$ or $[Rh(COD)Cl]_2$ in excess did not have an effect on the EPR spectra on the time scale of hours. In the functionalizations with $C(C_6H_5)_3^+$, the reactions were complete upon mixing for the corroles but slower and requiring minutes for completion (at ca. 10^{-4}−10^{-5} M solutions) for the higher generations of dendrimers.

The chromium(V)−nitrido−corrole dendrimers were studied in pure CH_3NO_2 and in $MeNO_2$/DMF mixtures. In pure CH_3NO_2, the spectra were similar (slightly broader; Figure 3a−c) to the spectra obtained for complexes of simple corroles (Figure 2a).

The sharp EPR signals obtained for all generations of dendrimers in CH_3NO_2 indicate a fast tumbling of the dendrimers on the EPR time scale.[23] Addition of a small amount of DMF caused a significant change in the EPR spectra. This is illustrated in the upper part of Figure 3, where EPR spectra of the middle-sized chromium(V)−nitrido−corrole dendrimer (**9**) is shown in mixtures of the two solvents. Significant freezing of the spectra

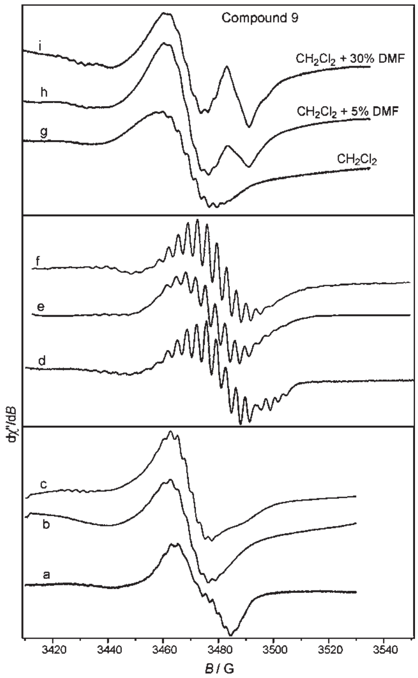


Figure 3. (a−c) EPR spectra in CH_3NO_2 of the three generations of chromium(V)−nitrido-functionalized corrole dendrimers. (d−f) Spectra of the same systems reacted with excess tritylhexafluorophosphate. (g−i) Spectra of the corrole dendrimer (**9**) complexed with chromium(V) nitride in neat CH_2Cl_2 and with added DMF.

was observed when DMF was added, indicating a change of the dendrimer structure in solution. Interpretation of the extra signal at high field as one component (the perpendicular) of an anisotropic spectrum overlaid with the isotropic spectrum requires that $g_\| > g_\perp$, an assumption which is corroborated by the frozen-solution spectrum of the chromium(V)−nitrido corrole ester complex (Supporting Information). This effect can be ascribed to the breaking of intramolecular hydrogen bonding in the dendrimer structure. The increase in the size accompanying this swelling reduces the tumbling rate and causes a freezing of the signal on the EPR time scale. The effect is observed for all generations but becomes much less pronounced with increasing size.

In conclusion, we have presented the synthesis of the first corrole-centered dendrimers via a convergent route. Access to the dendrimer cores has been demonstrated by the metal complex formation of the assembled dendrimers and subsequent atom-transfer chemistry to yield chromium(V)−nitrido-derivatized systems. The occurrence of this atom-transfer reaction at the inner sphere of the chromium(III)−corrole shows that the dendrimer core is accessible to a bulky, uncharged $Mn^V(N)$salen complex. Further, the bridge formation at the centrally coordinated chromium(V) center was achieved by reaction with the trityl cation, as is unambiguously shown by EPR spectroscopy. The sensitivity of the hyperfine coupling in $Cr^V(N)$ toward functionalization in combination with its diverse reactivity renders it a possibly very versatile spin probe also for related porphyrin- or corrin-centered systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. General experimental procedures, UV/vis spectra, and EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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