that pattern with $k_{H_2O_2}/k_{ROOH}$ typically 3-5.[20,26] Perhaps it is better to compare the composite of constants k_3k_4/k_{-3} for the VO^{2+} reactions. This composite represents the net reaction flux through both steps and is thus comparable to the "simple" bimolecular rate constants for Cr^{2+} and V^{2+} where peroxide binding and peroxide cleavage steps are not separated. The values for VO^{2+} are 0.21 (H_2O_2), 1.1 (*t*-BuOOH), and 1.0 (*t*-AmOOH). The statistical factor is not evident—indeed, it is reversed—but the reactivities are more comparable than would be concluded from k_1 values alone.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

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Electron-Transfer-Induced Isomerization η^2(C=C) → η^1(N) of the Tetracyanoethylene Complex $(C_6N_4)W(CO)_5^{0/\bullet-}$

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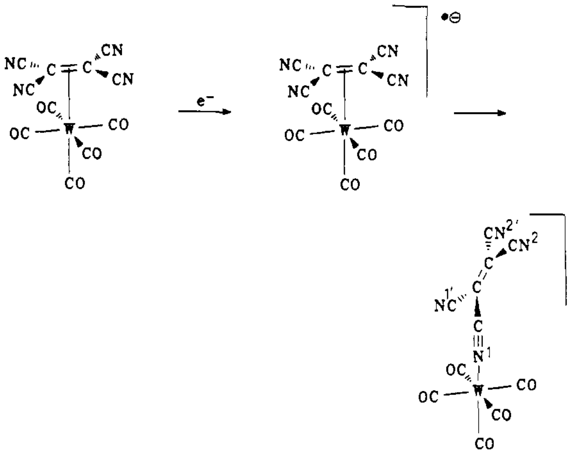
Received November 7, 1991

Single-electron transfer to the π(C=C)-bonded tetracyanoethylene (TCNE) ligand in the blue complex with $W(CO)_5$ leads to a yellow isomerized anion-radical product in which $TCNE^{\bullet-}$ coordinates via one nitrile nitrogen lone pair. The high-resolution EPR, UV/vis, and infrared data of the singly reduced complex clearly illustrate the lowered symmetry and diminished π-back-donation in the anionic form. Cyclic voltammetric experiments at variable scan rates show two distinctly separate second reduction processes of the π- and σ-coordinated complexes in what appears to be an organometallic example of "molecular hysteresis" (Sano, M.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 2327).

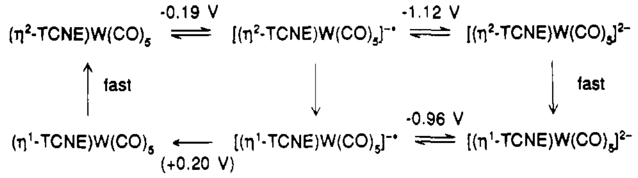
Introduction

Cyanoolefins, and especially tetracyanoethylene (TCNE), have long been recognized as ambidentate ligands toward metal centers.[1-4] Both the electron-acceptor-substituted C=C bond and the N lone pairs of the nitrile functions are well established to coordinate inorganic and organometallic 16-valence-electron complex fragments.[1-3] Whereas hard-metal centers prefer the σ(N) coordination mode,[2] "soft" and π-electron-rich organometallics prefer the π(olefin) coordination.[1] The prediction of the type of coordination mode is not always easy, as the reformulation of $(C_5R_5)(CO)_2Mn(TCNE)$ from a π(C=C)-[4a,b] to a σ(N)-coordinated complex has shown.[3,5] In this contribution we present detailed electrochemical and spectroscopic evidence for the coordination of the $W(CO)_5$ fragment by TCNE in both ways, depending on the *oxidation state* of this ligand (1).[6]



(1)

Scheme I



Experimental Section

The synthesis of blue $(C_6N_4)W(CO)_5$ was described previously.[3,4] The singly reduced form was preferably generated as a yellow persistent species in polar but noncoordinating acetone via addition of KBH_4 or *n*-Bu_4NBH_4. In a typical experiment, a solution of 500 mg (1.1 mmol) of (TCNE)$W(CO)_5$ in 50 mL of acetone was combined with a 385-mg (1.5 mmol) amount of *n*-Bu_4NBH_4 at room temperature. The yellow-brown solution formed was kept for 48 h at −30 °C. Concentration of this solution by removal of solvent in vacuo gave a dark, noncrystalline, and air-sensitive material which could not be redissolved in acetone and was not characterized further.

Instrumentation. For cyclic voltammetry a Princeton Applied Research potentiostat/function generator 273/175 and a three-electrode configuration with glassy-carbon working electrode, Pt counter electrode, and Ag/AgCl as reference were used. Internal calibration was done with the ferrocene/ferrocenium pilot system in dichloromethane/0.1 M *n*-Bu_4NPF_6. For EPR measurements a Bruker spectrometer ESP 300 in the X band was used. *g* factors were determined by using a Bruker NMR gaussmeter ER035M and a HP 5350B microwave counter. Computer simulations of EPR spectra were performed using available programs.[7a] For IR spectrometry a Perkin-Elmer spectrometer 684 was employed, and for UV/vis a Bruins Instruments spectrometer Omega 10 was used.

HMO/McLachlan perturbation calculations of π spin populations ρ were carried out using standard routines[7b,9] with the parameters h_N =

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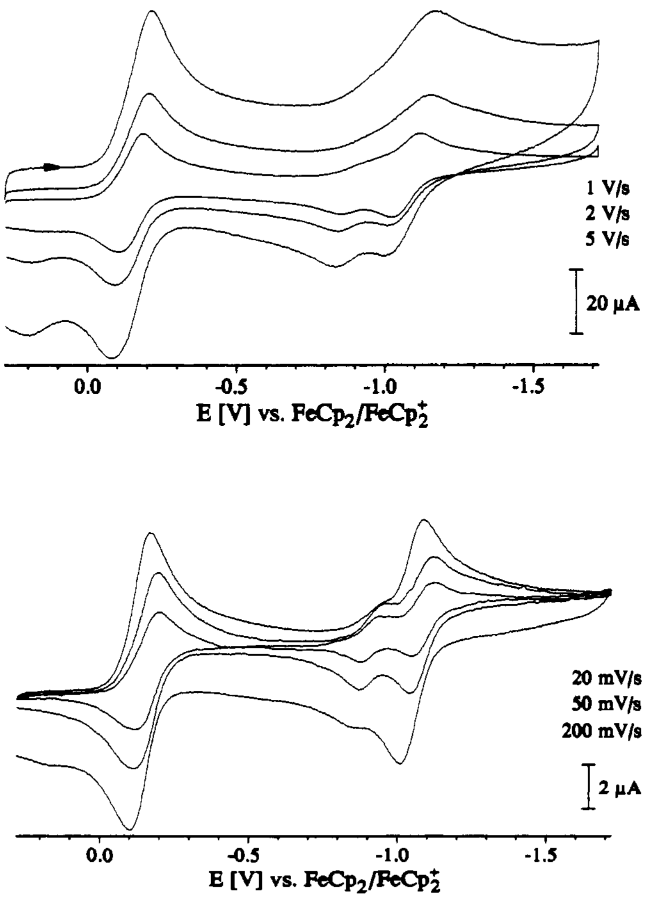

Figure 1. Cyclic voltammograms for the reduction of (TCNE)W(CO)$_5$ (5×10^{-3} M) in dichloromethane/0.1 M n-Bu_4NPF_6 at various scan rates.

0.5 (noncoordinating N centers), $0.5 < h_N^1 < 1.5$ (metal-coordinating N center), $h_C = 0.0$ (Coulomb integral parameters), and $k_{C\equiv N} = k_{C-C} = 1.0$ (resonance integral parameters) and the McLachlan parameter $\lambda = 1.2$.[9]

Results and Discussion

In dichloromethane/0.1 M Bu_4NPF_6, the neutral complex (η^2-TCNE)W(CO)$_5$ is reduced reversibly at −0.19 V vs Fc/Fc$^+$ (ΔE_{pp} 70 mV). This potential is rather close to that of free TCNE (−0.20 V), indicating considerable π-back-donation in the ground state;[3] the difference is smaller here than in acetonitrile.[3] The position of the first reduction wave (Figure 1) remains unchanged within the range of applied scan rates (20–5000 mV/s).

The second reduction to the dianion is usually a reversible process for TCNE and its complexes;[3,8] however, there are now two such waves in the cyclovoltammograms, their ratio depending on the scan rate (Figure 1). At fast scan rates, one major wave is observed at a potential of −1.12 V vs Fc/Fc$^+$ (ΔE_{pp} 70 mV at 200 mV/s) which is, as expected,[3,8] 0.9–1.0 V more negative than the potential for the first reduction. There are two small additional reoxidation peaks at −0.85 V for the dianion and at +0.20 V for the anionic form (Figure 1), shifted positively relative to the main features. At slower scan rates, a secondary reversible wave (ΔE_{pp} 80 mV) appears for the second reduction at a potential of −0.96 V, which clearly grows at the expense of the primary second reduction wave (Figure 1). The small additional reoxidation peak for the anion at +0.2 V disappears at slower scan rates.

The electrochemical results indicate ECEC processes[6] within a double-square[6c,d] scheme (Scheme I) in which the first reduction produces a primary anionic species which is converted in a relatively slow chemical step ($t_{1/2} > 10$ s) to a secondary monoanionic product, as evident from two competing second reduction processes to two different dianions. Whereas the reoxidation of the rapidly formed ($t_{1/2} < 1$ s) secondary dianion is always observable at about −0.85 V within the range of scan rates employed, the reoxidation of the monoanionic species to the established neutral (η^2-) form occurs predominantly at a single half-wave potential of −0.19 V for a reversible process; only at rather high scan rates is a small additional anodic peak detectable for the irreversible reoxidation of the secondary monoanionic species at +0.20 V (Figure 1), corresponding to a fast process ($t_{1/2} < 0.1$ s). Previous studies have focused on the first reduction process at moderate scan rates and could thus not reveal the more complicated reaction pattern.[3]

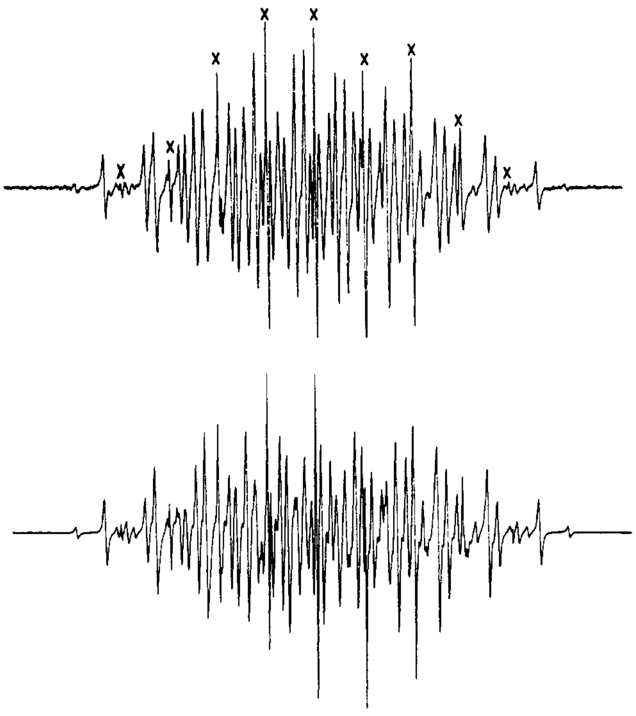

Figure 2. (Top) EPR spectrum of a 10^{-5} M acetone solution of (TCNE)W(CO)$_5$, reduced with solid KBH_4. (Bottom) computer-simulated spectrum, consisting of (TCNE$^{\bullet-}$)W(CO)$_5$ and a small amount of noncoordinated TCNE$^{\bullet-}$ (X). The simulation was carried out using the data given in the text and line widths of 0.0075 mT (complex) and 0.0051 mT (TCNE$^{\bullet-}$, a_N 0.158 mT, no ^{13}C coupling included).

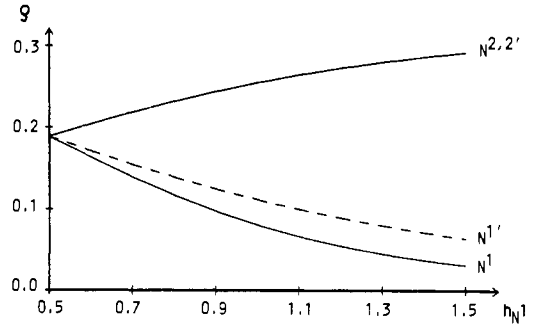

Figure 3. π spin populations ρ at the four different nitrogen centers of the N^1-perturbed TCNE anion radical (1) from HMO/McLachlan calculations.

An interpretation of the qualitative electrochemical Scheme I for "molecular hysteresis"[6d] is possible by studying the EPR spectrum of the long-lived secondary anionic species. On chemical reduction with KBH_4 in acetone (a "slow" process when compared to cyclic voltammetry), a line-rich spectrum is obtained (Figure 2) which exhibits some noncoordinated TCNE$^{\bullet-}$ (g 2.00263, a_N 0.158 mT) as a minor dissociation product and a main species, centered at g 2.00251, with one small, one large, and two intermediate ^{14}N coupling constants and a ^{183}W isotope coupling of 0.187 mT (^{183}W: $I = ^1/_2$, 14.3% natural abundance).

Such a splitting pattern is only compatible with an unsymmetrical, σ(N)-coordinated TCNE anion radical in a complex

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[9] Gerson, F. *High Resolution E.S.R. Spectroscopy*; Wiley: New York, 1970.

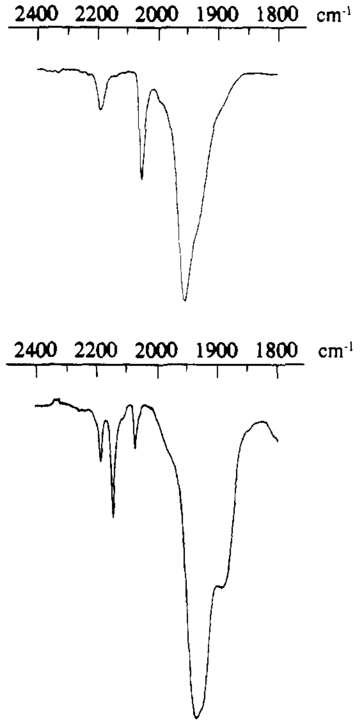

Figure 4. Infrared spectra of neutral (TCNE)W(CO)$_5$ (A, top) and of the long-lived singly reduced form (B, bottom) in about 10^{-3} M acetone solutions.

(η^1-TCNE$^{\bullet-}$)W(CO)$_5$. In fact, a Hückel MO/McLachlan perturbation calculation[9] on σ(N)-perturbed TCNE$^{\bullet-}$ indicates an identical increase of π spin populations at the two "remote" nitrile in π centers N$^{2,2'}$ and a virtually parallel decrease at the coordinated (N^1) and "geminal" nitrile nitrogen atom N$^{1'}$ (Figure 3).

Increasing the Coulomb integral parameter at coordinating π centers has proven to be a convenient way to simulate the effect of metal coordination on relative orbital energies and π spin populations.[10] Since the mere coordination of a transition-metal center can produce an increased nitrogen coupling constant, regardless of the spin density change,[10] we assign the large coupling constant of 0.246 mT to metal-coordinated N^1, the small coupling constant of 0.134 mT to N$^{1'}$, and the intermediate coupling constant of 0.166 mT for two "equivalent" nuclei to N$^{2,2'}$. This interpretation for an anionic compound is in agreement with the assignments made for neutral and cationic η^1-TCNE$^{\bullet-}$ complexes.[8b,11]

Infrared vibrational and UV/vis absorption data as obtained after "slow" chemical reduction support the interpretation of (CO)$_5$W(η^1-TCNE) as the long-lived secondary product of the reduction of the neutral precursor.

Whereas π(C=C)-coordinated complexes of TCNE in various oxidation states of this ligand exhibit only one nitrile stretching band in the IR region (cf. Figure 4A),[1,3,12] there are now two major bands for the persistent reduced form at 2182 and 2140 cm^{-1} (Figure 4B). Relative to the C≡N stretching frequencies of 2223 and 2171 cm^{-1}, as determined by resonance Raman spectroscopy[12] for the neutral π-coordinated precursor, the values of the σ-coordinated reduced species are shifted to lower energies.

Furthermore, the high-energy a$_1$ band for the totally symmetric CO stretching vibration at 2070 cm^{-1} is rather weak in the reduced σ complex with its more octahedral, *hexa*coordinated metal center; for the neutral π-coordinated species with an effectively *hepta*-coordinated metal, the corresponding band at 2060 cm^{-1} has a higher IR intensity (Figure 4). The larger spacing of CO stretching bands in the reduced complex ($\Delta\tilde{\nu}_{CO}$ 180 cm^{-1}) relative to the neutral form ($\Delta\tilde{\nu}_{CO}$ 125 cm^{-1}) is an indication[13] of diminished π-back-bonding of the non-carbonyl ligand.

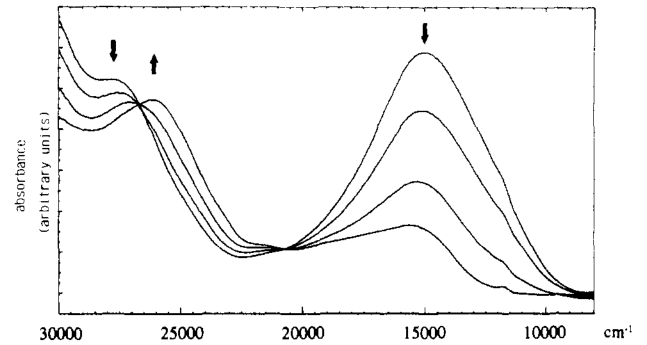

Figure 5. Changes of the UV/vis absorption spectra of a 10^{-5} M acetone solution of (TCNE)W(CO)$_5$ (ϵ 5100 M^{-1} cm^{-1} at 15 000 cm^{-1}) on slow reduction with a suspension of KBH$_4$.

Table I. Summary of Electrochemical and Spectroscopic Data

	(η^2-TCNE)W(CO)$_5$ olefin π coordination	(η^1-TCNE)W(CO)$_5$ nitrile N σ coordination
E_{red1}[a]	−0.19	(+0.20, E_{pa})
E_{red2}[a]	−1.12	−0.96
		[(η^1-TCNE)W(CO)$_5$]$^{\bullet-}$
$\tilde{\nu}_{max}$[b,c]	14 950	26 000
	27 770	
$\tilde{\nu}$(CN)[b,c]	2195 (m)	2182 (w)
		2142 (m)
$\tilde{\nu}$(CO)[b,c]	2060 (m)	2070 (w)
	1957 (vs)	1933 (vs)
	1935 (sh)	1890 (s)
	TCNE$^{\bullet-}$	
g[c]	2.002 63	2.002 51
a(^{14}N)[c,d]	0.158 (4 N)	0.246 (1 N)
		0.166 (2 N)
		0.134 (1 N)
a(^{183}W)[c,d]		0.187 (1 W)

[a] Half-wave potentials in V vs Fc/Fc$^{\bullet+}$, unless specified otherwise. Measurements in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$, peak potential differences are dependent on the scan rate (Figure 1). [b] In cm^{-1}. [c] Measurements in acetone solution. [d] EPR coupling constants in mT.

Slow reduction of blue (TCNE)W(CO)$_5$ with its absorption maxima at 14 950 and 27 770 cm^{-1} by a suspension of KBH$_4$ in acetone as followed by UV/vis spectroscopy results in a series of spectra exhibiting two clear isosbestic points at 21 000 and 26 700 cm^{-1} (Figure 5). The long-wavelength absorption maximum of the yellow secondary reduction product lies at 26 000 cm^{-1}; however, this band is not vibrationally structured as that in free TCNE$^{\bullet-}$ ($\tilde{\nu}_{max}$ 23 360 cm^{-1}).[14] The hypsochromic shift of this HOMO → SOMO transition[14] upon metal coordination is supported by HMO perturbation calculations[8b] which show an increase of the HOMO–SOMO gap upon increasing the Coulomb integral parameter at one nitrogen center. All electrochemical and spectroscopic data are summarized in Table I.

The $\pi \rightarrow \sigma$ isomerization upon reduction and the fast $\sigma \rightarrow \pi$ rearrangement on reoxidation of (CO)$_5$W(TCNE$^{0/-}$) as evident from cyclic voltammetry can occur in an inter- or intramolecular fashion. Even in the latter case, a small amount of dissociation could occur along the reaction pathway; the appearance of such a dissociation product in the form of free TCNE$^{\bullet-}$ (Figure 2) does not rule out an intramolecular process.

The driving force behind the isomerization in Scheme I lies in the requirement for bonding of W(CO)$_5$: A (weakly) nucleophilic *and* π-accepting site is needed for π coordination according to the Dewar–Chatt–Duncanson model (2).

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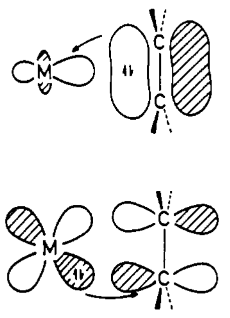

(2)

Upon reduction of TCNE, the C=C-centered π^*-acceptor orbital becomes singly occupied (LUMO → SOMO); thus, the effectiveness of d(metal)-to-π^*(olefin) back-bonding is diminished. On the other hand, the negative charge acquired on reduction turns TCNE$^{\bullet-}$ into an acceptable ligand of different character; the relatively long range of electrostatic interactions makes a coordination via the nitrile N lone pair more attractive. In fact, all known complexes in which TCNE is bound in the anion-radical oxidation state are either η^1-coordinated[2,3,8,11] or, in the case of coordinatively saturated metal components, form charge-transfer materials with noncoordinated TCNE$^{\bullet-}$.[15] Both positive shifts of the reduction potentials for the σ(N)-bonded isomers as well as the increased energetic splitting of carbonyl stretching frequencies of the coordinated W(CO)$_5$ after reduction are in agreement with diminished π-back-donation in this persistent secondary σ(N)-coordinated form.

Summarizing, we have presented an example for electron-transfer-induced isomerization which is distinguished both by a change of hapticity[6] of the metal *and* by a change of the type of donor atoms.[16,17] Although this isomerization represents a qualitatively significant structural change, it does not become apparent from cyclic voltammetric studies of the corresponding redox process at conventional scan rates. Extension of the potential range, variation of scan rates, and use of several spectroscopic methods proved to be necessary to detect and clarify the organometallic molecular hysteresis[6d] process (1).

Acknowledgment. This work was supported by grants from Deutsche Forschungsgemeinschaft, Volkswagenstiftung, and Fonds der Chemischen Industrie. We also thank Walter Matheis and Michael Moscherosch for their help with the HMO/McLachlan and EPR simulation programs.

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Nuclear Magnetic Resonance Study of the Molecular and Electronic Structure of Nickel(II) Tetraphenyl-21-thiaporphyrins[†]

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Received May 8, 1991

The proton NMR spectra of high-spin ($S = 1$) nickel(II) monohalide complexes of tetraphenyl-21-thiaporphyrin have been recorded and assigned by means of specific deuteration, methyl substitution, and line width consideration. The characteristic pattern of pyrrole (downfield) and thiophene resonances (upfield) has been established. The specific assignment of pyrrole resonances has been achieved by NOE measurements. Replacement of chloride by perchlorate results in formation of low-spin diamagnetic complex Ni^{II}(STPP)ClO$_4$ in chloroform. Imidazole replaces the axial halide ligand to produce five-coordinate derivatives that give resonances for the coordinated axial ligand. The formation of the six-coordinate form has been also established. It is apparent from the ^{1}H NMR studies of Ni^{II}(STPP)Cl and related systems that the 21-thiaporphyrin macrocycle is flexible in solution. The structure of the equatorial macrocycle adjusts to the spin and electronic state of the Ni^{II}(STPP) moiety, as determined by the nature and number of axial ligands. The pyrrole shift pattern has been related to the Ni(II) coordination number. The isotropic shifts of pyrroles and thiophene resonances are dominated by the σ-contact mechanism. The direct σ–π spin density transfer has been proposed to explain the upfield shift of the thiophene and a large difference in contact shifts of pyrrole resonances even for protons located in the same pyrrole ring. To account for the sulfur contribution and the geometry of 21-thiaporphyrin, the semiquantitative Fenske–Hall LCAO MO method has been used to determine molecular orbitals involved in the distribution of spin density via π-orbitals.

Introduction

Although porphyrins and related pyrrole compounds are among the most widely studied of all known macrocycles,[1] relatively little effort has been devoted to the development of macrocyclic systems where modification of porphyrin has been achieved by introduction of other donors (O, S, Se, NCH$_3$, NO, N–C) to replace one or more pyrrole nitrogens.[2–5] These new macrocycles are of interest as potential complexing agents. Limited reports on the oxaporphyrins, dithiaporphyrins, and diselenaporphyrins have appeared.[6] The tetraoxaporphyrin dication has recently been

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* To whom correspondence should be addressed.

[†] Abbreviations: STPP, 5,10,15,20-tetraphenyl-21-thiaporphyrin anion; STTP, 5,10,15,20-tetrakis(*p*-tolyl)-21-thiaporphyrin anion; STPP-d_{10}, 5,20-diphenyl-10,15-bis(phenyl-d_5)-21-thiaporphyrin anion; STPP-d_6, 5,10,15,20-tetraphenyl-21-thiaporphyrin anion deuterated at pyrrole β-positions.

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