

reactions appear to be inversely proportional to the electron richness of the Cr centers. If all these observations are taken together, this trend in the rate of decomposition of the generated radical cations is consistent with that in the $E^{\circ'}$ and $\nu_{\text{CO}}(\text{Cr}(\text{CO})_3)$ values of the parent complexes and is a reflection of the electron-transfer abilities of the arene and Fp groups.

It is evident from this work that polymetalation of the arene in the title complexes leads to remarkable stability of their respective radical cations, even in a coordinating solvent such as acetonitrile. Experiments to obtain the stable radical cations of all of the title complexes and to elucidate the origin of this stabilization are currently in progress.

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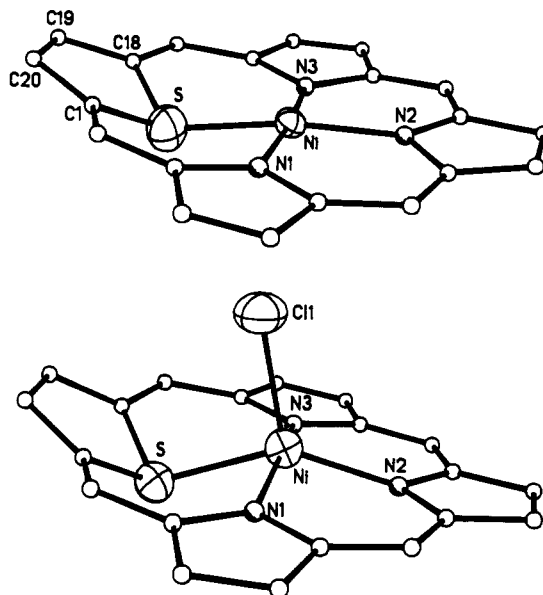


Figure 1. Comparison of the thiaporphyrin inner cores (phenyl and *p*-tolyl groups omitted) for (top) Ni^I(SDPDTP) and (bottom) Ni^{II}(STTP)Cl.

The First Structural Characterization of a Nickel(I) Macrocyclic System: Structure of Nickel(I) Diphenyldi-*p*-tolyl-21-thiaporphyrin

Factor F₄₃₀ (1), the prosthetic group of methyl-coenzyme M reductase, contains nickel ion in a macrocycle with N₄ coordination.¹ Observation of an ESR signal in whole cells of *Meth-*

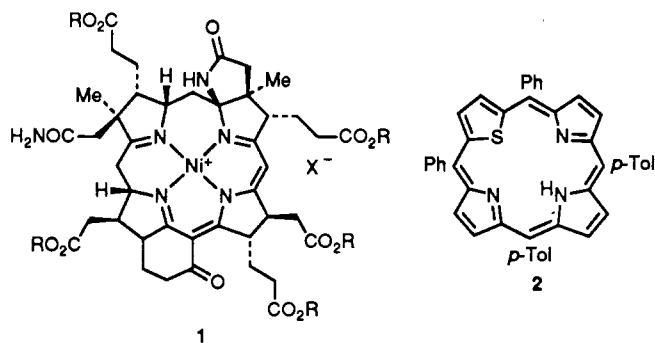


Table I. Characteristic Distances (Å) and Angles (deg)

	Ni ^I - (SDPDTP)	Ni ^{II} - (STTP)Cl ^d	Cu ^{II} - (STTP)Cl ^d
Distances			
M-N(1)	2.015 (12)	2.094 (3)	2.055 (6)
M-N(3)	2.014 (12)	2.084 (3)	2.057 (7)
M-N(2)	1.910 (14)	1.963 (4)	1.962 (8)
M-S	2.143 (6)	2.296 (1)	2.335 (2)
M-N ₃ ^a	0.042	0.295	0.274
Angles			
S-M-N(2)	170.6 (4)	146.0 (1)	144.4 (2)
N(1)-M-N(3)	173.2 (6)	162.8 (1)	163.7 (2)
C(1)-S-C(18)	92.9 (9)	92.4 (5)	91.3 (5)
C(1)-S-M	119.4 (6)	107.6 (1)	106.3 (3)
C(18)-S-M	118.0 (7)	108.6 (1)	107.3 (3)
C ₁ SC ₁₈ vs M-S ^b	45.9	63.3	65.6
C ₁ C ₁₈ C ₁₉ C ₂₀ vs C ₁ SC ₁₈ ^c	14.6	13.4	14.7

^a Distance of the metal from the N₃ plane. ^b Angle between the M-S line and the C₁SC₁₈ plane. ^c Angle of folding of the thiophene ring. ^d Data from ref 6.

anobacterium thermoautotrophicum has been attributed to Factor F₄₃₀ in the intact, active enzyme, and the *g* values and hyperfine coupling constants of this signal are consistent with the presence of Ni^I (or Ni^{III}).² Reduction of factor F₄₃₀ pentamethyl ester has been shown to yield a reduced species (*g* = 2.065, 2.074, 2.250) in which reduction is localized on the metal and the tetrahydro-corphin ring system is unaltered.³

It has generally been assumed that reduction of Ni^{II} within a macrocycle would lead to expansion of the Ni-ligand distances.⁴⁻⁷

In considering the redox potentials for a wide range of Ni^{II} tetraaza macrocycles, Busch and co-workers⁴ noted a correlation with core size and reasoned that larger cores better accommodate the (presumably) larger Ni^I and facilitated reduction. In examining the causes for varying degrees of unsaturation in biological macrocycles (e.g. porphyrin, chlorin, hydrocorphin), Stolzenberg and co-workers⁵ have focused on hole size differences as determining the relative stability of different metal ion oxidation states and have estimated that a Ni^I-N distance would be optimal in excess of 2.1 Å. Here we report on the structure of a Ni^I complex of a macrocyclic ligand, diphenyldi-*p*-tolyl-21-thiaporphyrin (2, (SDPDTP)H), that allows determination of Ni-N distances within this environment along with direct comparison to a corresponding Ni^{II} complex, Ni^{II}(STTP)Cl (STTP is the monoanion of tetra-*p*-tolyl-21-thiaporphyrin).⁸

Brown, paramagnetic (*g* = 2.030, 2.040, 2.109 in frozen toluene) crystals of Ni^I(SDPDTP) were obtained as described previously⁹

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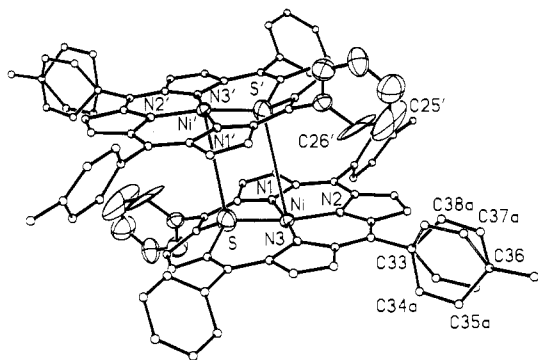


Figure 2. Drawing showing the interaction between adjacent, centrosymmetrically related $\text{Ni}^{\text{I}}(\text{SDPDTP})$ molecules. The disorder in one phenyl ring and large thermal parameters for C(25) and C(26), presumably due to short intermolecular contacts, are also illustrated. Atoms drawn as circles were refined with isotropic thermal parameters and are given an arbitrary size. The solid lines connecting Ni and S' and Ni' and S do not represent conventional chemical bonds.

from $\text{Ni}^{\text{II}}(\text{SDPDTP})\text{Cl}$ by reduction with aqueous sodium dithionite and crystallized by diffusion of acetonitrile into a benzene solution of the complex. The core structure, as determined by X-ray crystallography, is shown in Figure 1 along with that of $\text{Ni}^{\text{II}}(\text{STPP})\text{Cl}$.⁸ Relevant structural parameters, along with those for $\text{Ni}^{\text{II}}(\text{STPP})\text{Cl}$ and $\text{Cu}^{\text{II}}(\text{STPP})\text{Cl}$,⁸ are presented in Table I. The geometry of $\text{Ni}^{\text{I}}(\text{SDPDTP})$ resembles that of other thiaporphyrin complexes with the thiophene ring tipped 52.3° out of the N_3 plane and pyramidal coordination of the thiophene sulfur.

The Ni^{I} ion has nearly planar geometry and *surprisingly short* Ni-N and Ni-S bonds. Comparison of the data in Table I indicates that the Ni-N and Ni-S bond lengths decrease upon reduction of high-spin ($S = 1$), five-coordinate $\text{Ni}^{\text{II}}(\text{STPP})\text{Cl}$ to four-coordinate ($S = 1/2$) $\text{Ni}^{\text{I}}(\text{SDPDTP})$. Additionally, the Ni-N and Ni-S distances in $d^9 \text{Ni}^{\text{I}}(\text{SDPDTP})$ are shorter than those in five-coordinate, $d^9 \text{Cu}^{\text{II}}(\text{STPP})\text{Cl}$. The $\text{Ni}^{\text{I}}\text{-N}$ distances are also shorter than the $\text{Ni}^{\text{II}}\text{-N}$ distances (2.024, 2.052 Å) in a high-spin, six-coordinate Ni^{II} porphyrin.¹¹ Moreover, the $\text{Ni}^{\text{I}}\text{-N}(2)$ distance is shorter than the $\text{Ni}^{\text{II}}\text{-N}$ distances (1.92–1.96 Å) in four-coordinate, diamagnetic Ni^{II} porphyrins^{12,13} while the $\text{Ni}^{\text{I}}\text{-N}(1)$ and $\text{Ni}^{\text{I}}\text{-N}(3)$ distances are longer. Similarly, the $\text{Ni}^{\text{I}}\text{-N}(2)$ distance is shorter and the $\text{Ni}^{\text{I}}\text{-N}(1)$ and $\text{Ni}^{\text{I}}\text{-N}(3)$ distances are longer than the $\text{Cu}^{\text{II}}\text{-N}$ distance (1.981 (7) Å) in the four-coordinated $d^9 \text{Cu}^{\text{II}}$ (tetraphenylporphyrin).¹⁴

Comparison of the Ni^{II} and Ni^{I} structures clearly shows that reduction does not necessarily imply expansion of metal-ligand distances. In cases where the coordination number is lowered, a lack of expansion upon reduction is a fairly general phenomenon that is maintained, for example, in the following pairs: $\text{Ni}^{\text{II}}(\text{PMe}_3)_2\text{Br}_2$, $\text{Ni}^{\text{II}}\text{-P} = 2.19\text{--}2.20$ Å;¹⁵ $\text{Ni}^{\text{I}}(\text{PMe}_3)_4^+$, $\text{Ni}^{\text{I}}\text{-P} = 2.211\text{--}2.221$ Å;¹⁶ $\text{Cu}(2,5\text{-dithiahexane})_2(\text{ClO}_4)_2$, $\text{Cu}^{\text{II}}\text{-S} = 2.320\text{--}2.354$ Å; $\text{Cu}(2,5\text{-dithiahexane})_2(\text{ClO}_4)_2$, $\text{Cu}^{\text{I}}\text{-S} = 2.263$ Å;¹⁷

$\text{Cu}(3\text{-methoxy-1,5-dithiacyclooctane})_2^{2+}$, $\text{Cu}^{\text{II}}\text{-S} = 2.294\text{--}2.351$ Å;¹⁶ $\text{Cu}(3\text{-methoxy-1,5-dithiacyclooctane})_2^+$, $\text{Cu}^{\text{I}}\text{-S} = 2.346$ Å.¹⁸ There also are examples in which reduction without ligand loss is accompanied by a decrease in metal-ligand distances. These include the four-coordinate iron porphyrins with formal oxidation states of Fe^{II} , Fe^{I} , and Fe^0 ¹⁹ and the corresponding cobalt complexes with formal oxidation states Co^{I} and Co^0 .^{20,21} In these cases the structures have been interpreted to indicate a significant degree of porphyrin reduction. Evidence for predominant, metal-based reduction for **2** in solution has been presented.⁹ Attempts are in progress to obtain a four-coordinate Ni^{II} thiaporphyrin complex so that a comparison can be made of Ni^{II} and Ni^{I} without a change of coordination number. The dramatic shortening of the Ni-S bond that occurs upon reduction may reflect increased π back-donation as suggested previously for Cu-S bonds.^{16,17} It remains to be seen whether the presence of the sulfur atom in $\text{Ni}^{\text{I}}(\text{SDPDTP})$ plays a role in producing the short Ni-N bonds seen here.

Figure 2 shows the interaction of a pair of $\text{Ni}^{\text{I}}(\text{SDPDTP})$ molecules within the crystal. The intermolecular Ni-S' contacts (shown as solid lines) are quite long (4.106 (6) Å), and the nickel ions lie on the side of the thiaporphyrin plane that is opposite the neighboring sulfur. Consequently, the Ni-S interaction is weak and is of minor importance to the geometry of the molecule. However, it probably is a major component involved in the antiferromagnetic behavior of the solid ($\mu = 2.28 \mu_B$ (per Ni) at 295 K and $0.71 \mu_B$ at 2 K). Contact between molecules also leads to disorder in the positions of two phenyl rings. Notice that in Figure 2 the phenyl ring involving C(21)–C(26) is close to the *p*-tolyl ring containing C(33)–C(38). These contacts lead to two alternate positions for the *p*-tolyl ring and large amplitudes for thermal parameters for the phenyl ring C(21)–C(26).

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Supplementary Material Available: A table of crystal data, a fully labeled drawing, and tables of positional parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom positions (8 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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- (10) Dark-brown plates of $\text{Ni}^{\text{I}}(\text{SDPDTP})\text{-CH}_3\text{CN}$ belong to the space group $P2_1/c$ with $a = 15.746$ (6) Å, $b = 15.944$ (4) Å, $c = 15.472$ (6) Å, $\beta = 113.25$ (3)°, and $Z = 4$ at 130 K. Refinement yielded $R = 0.077$ for 1585 reflections with $I > 3\sigma(I)$ and 273 parameters. There is disorder in the carbon atoms of two phenyl rings. In one case (C(33)–C(38)) the disorder could be modeled by the assignment of two equally probable positions of the phenyl ring, one rotated with respect to the other. In the other case (C(21)–C(26)) it could be only modeled by assuming anisotropic thermal motion.
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Aromatic Ring Stacking in Ternary Copper(II) Complexes [Cu(histamine)(L-AA)(ClO₄)] (AA = Phenylalaninate, Tyrosinate). Structural Evidence for Intramolecular Stacking Involving a Coordinated Imidazole Ring

Biological molecular recognition is achieved by combination of various noncovalent interactions.¹ Aromatic ring stacking has