and phlorin formation that slows down or does not occur at low temperatures. A broad absorbance band appears around 820 nm during the second reduction of (T(p-Et_2N)PP)Ni while weak bands emerge at 520 and 620 nm (see Figure 10b). This type of spectrum corresponds to a phlorin anion.[16,38]

The spectral changes in Figure 10c were obtained when the applied potential was set at 0.9 V. Both the changes in the Soret band region and the strong absorptions at wavelengths above 750 nm suggest a delocalization of charge over two of the four diethylamino groups. The final oxidation product of (T(p-Et_2N)PP)Ni is not ESR active, and the UV–visible spectrum is similar to that obtained after the two-electron oxidation of the same compound in CH_2Cl_2.[2]

Spectra recorded during the second oxidation of (T(p-Et_2N)PP)Ni are shown in Figure 10d and indicate a decreased band at 507 nm and an increased absorption band at 446 nm. The absorption bands at wavelengths greater than 750 nm decrease in intensity as all four diethylamino groups are oxidized. A catalytic oxidation of DMF also occurs at room temperature (see cyclic voltammogram at 24 °C in Figure 8) and results in generation of a porphyrin species with a Soret band at 446 nm and no broad bands between 750 and 950 nm.

Effect of the Porphyrin Macrocycle Basicity on Reversible Reduction Potentials. Substituent effect on porphyrin redox reactions have often been expressed by plots of $E_{1/2}$ vs. σ where σ is a measure of the electron-donating or electron-withdrawing substituent on the porphyrin ring.[28] The $E_{1/2}$ for reduction of free-base porphyrins to their radical anions in DMF solutions has been also used as a measure of porphyrin ring electron basicity[17] and is utilized in this present study for evaluating substituent effects.

Figure 11 shows the relationship between $E_{1/2}$ for the first and second reduction of the nickel porphyrins vs $E_{1/2}$ for reduction of the corresponding free base porphyrins in DMF. [T(p-Et_2N)PP]H_2 and (TPP)Ni are insoluble in DMF, and values of $E_{1/2}$ were measured in PhCN or in a mixture of benzene and DMF, respectively. The exact conditions and a list of half-wave potentials are given in Table II.

Half-wave potentials for the first reduction of a given nickel(II) porphyrin at the π ring system are generally more negative by 100–200 mV than $E_{1/2}$ for reduction of the corresponding free base porphyrin.[28] However, $E_{1/2}$ for the first reduction of (TpyP)Ni (−0.45 V) is 410 mV less negative than $E_{1/2}$ for the first reduction of (TpyP)H_2 (−0.86 V). The first reduction of (TpyP)Ni is also less negative than $E_{1/2}$ for the first reduction of positively charged [(TMpyP)Ni]$^{4+}$. A positive charge is not present in (TpyP)Ni, but $E_{1/2}$ values are similar to those for reduction of the easily reduced nickel(II) tri- and tetracyano-substituted tetraphenylporphyrins in DMF.[39] For example, the $E_{1/2}$ of −0.45 V is approximately midway between potentials for reduction of (TPP(CN)$_4$)Ni ($E_{1/2}$ = −0.330 V)[39] and (TPP(CN)$_3$)Ni ($E_{1/2}$ = −0.530 V)[39] in the same solvent system. On the basis of this comparison, one might predict that (TpyP)H_2 would also be reduced at an $E_{1/2}$ midway between values for reduction of (TPP(CN)$_4$)H_2 ($E_{1/2}$ = −0.120 V)[40] and (TPP(CN)$_3$)H_2 ($E_{1/2}$ = −0.330 V)[40] or at about −0.22 V. The actual $E_{1/2}$ value is −0.86 V. This latter value of $E_{1/2}$ for reduction of the free base complex is not unexpected, and the difference between the predicted and experimentally observed reduction potentials are thus actually associated with (TpyP)Ni rather than with (TpyP)H_2. This is evident from the data in Figure 11, which show deviations of 520 mV and 390 mV from linear plots involving the first and second reductions of (P)Ni and (P)H_2, respectively.

In summary, it is important to emphasize the unexpected demetalation of (TpyP)Ni after a two-electron reduction at the porphyrin π ring system. The metal ion size and geometry of the complex are not consistent with a demetalation. On the other hand, the unexpected facile reduction of the macrocyclic porphyrin ring is probably related to this demetalation, which leads to the ultimate formation of Ni(0) and a free base porphyrin in solution.

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Registry No. (TPP)Ni, 14172-92-0; [(TPP)Ni]$^-$, 88669-50-5; [(TPP)Ni]$^{2-}$, 112739-99-8; [(TMpyP)Ni]$^{4+}$, 48242-71-3; [(TMpyP)Ni]$^{3+}$, 112739-97-6; [(TMpyP)Ni]$^{2+}$, 112740-00-8; [(TMpyP)Ni]$^+$, 112763-16-3; [(TMpyP)Ni], 112763-17-4; (TpyP)Ni, 14514-68-2; [(TpyP)Ni]$^-$, 112739-98-7; [(TpyP)Ni]$^{2-}$, 112740-01-9; [(TpyP)Ni]$^+$, 112740-04-2; (T(p-SO_3Na)PP)Ni, 67204-04-0; [(T(p-SO_3Na)PP)Ni]$^-$, 112740-07-5; [(T(p-SO_3Na)PP)Ni]$^{2-}$, 112740-02-0; [(T(p-SO_3Na)PP)Ni]$^+$, 112740-05-3; [(T(p-SO_3Na)PP)Ni]$^{2+}$, 112740-06-4; (T(p-Et_2N)PP)Ni, 88669-48-1; [(T(p-Et_2N)PP)Ni]$^-$, 88669-57-2; [(T(p-Et_2N)PP)Ni]$^{2-}$, 112740-03-1; [(T(p-Et_2N)PP)Ni]$^+$, 88669-52-7; [(T(p-Et_2N)PP)Ni]$^{2+}$, 88669-62-9; TPyP, 16834-13-2; Ni, 7440-02-0.

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Kinetics and Mechanism of Electron-Transfer Reactions of Bis((−)-(*R*)-2-methyl-1,4,7-triazacyclononane)nickel(II) and -nickel(III) Complexes

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A synthesis of the title ligand ((−)-(*R*)-Me-9-aneN_3) is reported together with preparations of the nickel(II) and nickel(III) complexes. There is retention of an NiN_6 chromophore in both oxidation states. The nickel(II) species is very stable in aqueous media with a slow acid-catalyzed hydrolysis ($k_H = 1.8 \times 10^{-4}$ M^{-1} s^{-1} at 30 °C). The nickel(III) ion shows only slight decomposition at pH 3 and is indefinitely stable in acetonitrile. Rate constants for a series of outer-sphere electron-transfer reactions have been determined (with Co(phen)$_3^{2+}$ and I^- reducing Ni(III) and with Ni(cyclam)$^{3+}$, Ni(9-aneN_3)$_2^{3+}$, Ni^{IV}(oxime), and Co^{3+}(aq) oxidizing Ni(II)). Use of a Marcus cross-correlation leads to a self-exchange rate for the $NiL_2^{3+/2+}$ couple of (1.2 ± 0.5) × 10^4 M^{-1} s^{-1} (I = 1.0 M). The data are of interest in that there is retention of the octahedral symmetry at the metal center. Possible correlations of rates of electron exchange with bond extension in the inner coordination sphere are discussed.

Introduction

From being in a relatively rare oxidation state a decade ago, nickel(III) has become much more prominent as an accessible form[1-8] not only in polyaza macrocyclic complexes but also in several oligopeptide species[9,10] and biological systems, principally those involving methanogenic bacteria.[11-13] In the latter, there

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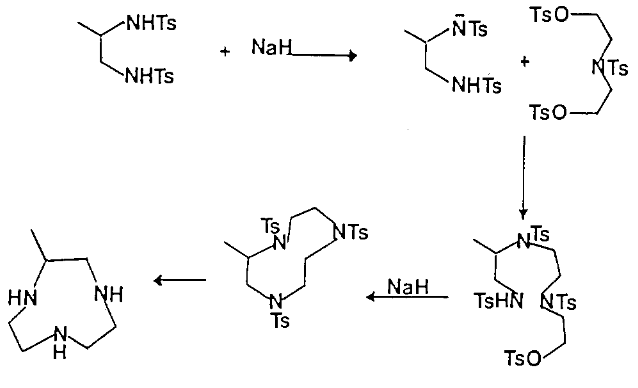
Scheme I



is thought to be redox activity associated with the metal center. Analysis of electron-transfer reactions in simpler systems is complicated in many instances, especially those involving tetraaza macrocyclic complexes, owing to the possible change in geometry between the generally square-planar $\mathrm{NiN_4}^{2+}$ systems and the pseudooctahedral nickel(III) centers. This problem has been addressed recently in the preparation of nickel oxime complexes[14-16] that incorporate an $\mathrm{NiN_6}$ chromophore in the nickel(II), -(III), and -(IV) states[8,17] and in the preparation of tris(bipyridyl)[18-20] and other di- and tervalent diimine complexes that retain octahedral geometry. Recently we[21] and others[22] have reported the preparation of bis(1,4,7-triazacyclononane)nickel(III) perchlorate (see Scheme I), the first example of a saturated $\mathrm{N_6}$ donor set that is relatively stable in aqueous media. The crystal structure of this species has been reported.[23]

In this paper, we have extended these studies with new syntheses of the *rac*- and (−)-(*R*)-2-methyl-1,4,7-triazacyclononane ligands and of the nickel(II) and nickel(III) complexes. We wish to extend investigations into the barriers associated with electron transfer, especially by studying whether the methyl groups in the nickel(III) bis complex may pose a structural impediment in the self-exchange reaction:

$$\mathrm{Ni^{II}L_2}^{2+} + {}^*\mathrm{Ni^{III}L_2}^{3+} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Ni^{III}L_2}^{3+} + {}^*\mathrm{Ni^{II}L_2}^{2+} \tag{1}$$

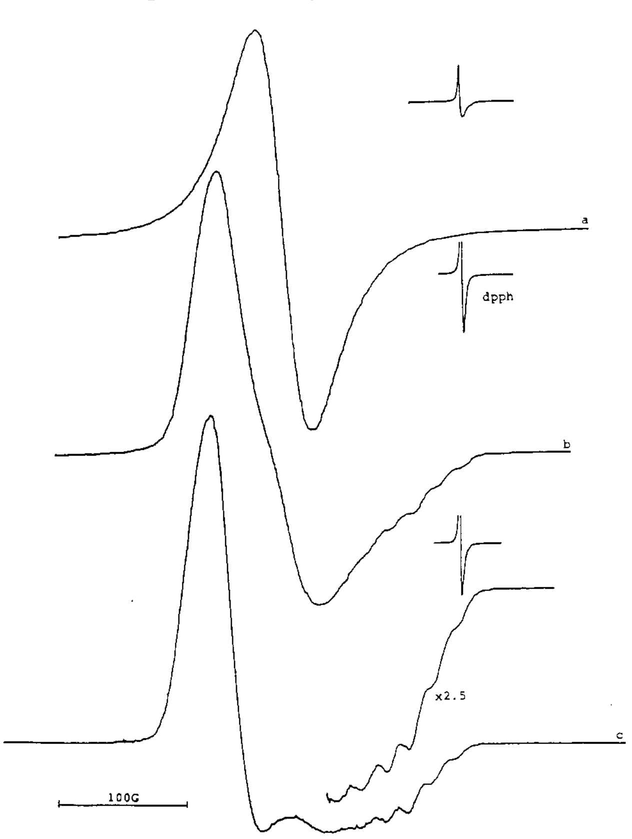


Figure 1. ESR frozen-solution (77 K) spectra, relatve to DPPH standard, of $\mathrm{Ni^{III}}$((−)-(*R*)-Me-9-$\mathrm{aneN_3)_2}^{3+}$ in (a) deionized water, (b) 0.1 M $\mathrm{LiNO_3}$, and (c) 3.0 M $\mathrm{HNO_3}$ (with 2.5× expansion).

Relatively few methods are available for determining directly the rate of electron transfer,[24] and the presence of an asymmetric center in one of the reactants may be of use[25,26] to provide the rate from optical rotation experiments. Unfortunately, reaction 1 is too rapid for use of this technique with the apparatus available to us. However, using cross-correlation reactions involving outer-sphere reagents, we have determined a value for the self-exchange parameters in the $\mathrm{NiL_2}^{2+/3+}$ couple.

Experimental Section

The ligand (−)-(*R*)-2-methyl-1,4,7-triazacyclononane ((*R*)-Me-9-$\mathrm{aneN_3}$) was prepared first as described in the literature.[27] However, better yields were obtained in a two-stage deprotonation of the tosylated propanediamine and cyclization to yield the tosylated macrocycle.

The free ligand (−)-(*R*)-diaminopropane was prepared (99.4% optical purity) by using the method of Dwyer and co-workers.[28] This was then N-tosylated and 0.1 mol (38.2 g) reacted in dimethylformamide with 0.1 mol of NaH (60% suspension in mineral oil) to yield the monosodium salt. After effervescence, the temperature was raised first to 70 °C and then to 110 °C, at which time 0.1 mol (56.7 g) of the tritosylate of ethanolamine was added dropwise with stirring. The solution was left for 1 h at this temperature. On cooling to 70 °C, a second 0.1 mol of sodium hydride was added and the temperature raised to 110 °C and maintained at this level for 4 h. On reduction in volume to 200 mL and addition to ice-cold water, the cyclic tritosylate precipitated. This could be recrystallized from methanol (34.4 g, 50% yield): mp 198 °C; mass spectrum *m*/*e* 605.

Detosylation (17.2 g) was carried out in concentrated sulfuric acid at 155 °C for 30 min, and then the solution was allowed to cool to room temperature. The mixture was dropped onto 300 mL of ice-cold ethanol (stirring) followed by addition of 1 L of diethyl ether. Filtration and removal of the organic layer and subsequent addition of concentrated HCl (75 mL) yielded the ligand trihydrochloride (4.3 g, 59%). Neu-

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tralization with base and continuous extraction into $CHCl_3$ provided the free ligand as a yellow oil: mass spectrum *m/e* 143; ^{13}C NMR 19.71 (Me), 51.70 (C_2), 50.96 (C_3), 46.08 (C_5), 46.99 (C_6, C_8), 44.28 ppm (C_9).

A similar procedure using 1,2-propanediamine gave the racemic ligand.

[Ni^{II}((-)-(*R*)-Me-9-aneN_3)$_2$](ClO_4)$_2$. A 1.01-g (4-mmol) sample of the ligand hydrochloride was dissolved in 12 mL of 1 M NaOH (0.012 mol), and the solution was warmed on a steam bath. Nickel(II) acetate (0.498 g, 2 mmol) was dissolved in 15 mL of methanol, and the mixture was added to the solution of the free ligand. The mixture was adjusted to pH 10.5 and warmed. It turned pink and was allowed to stand for 30 min. The pH was reduced to ~5 by using 1 M $HClO_4$ and on cooling (0 °C), purple crystals of the complex were obtained. A second crop was provided by adding saturated sodium perchlorate. In some preparations, prior to crystallization, the purple pH 5 solution was passed down a Sephadex G25 column. In this way two minor pink bands and any traces of free Ni^{2+} were removed. One trace band was eluted with water and the other with 0.45 M $NaNO_3$ following elution of the major product with nitrate (0.35 M). Anal. Calcd (found) for $NiC_{14}H_{34}N_6O_8$: C, 30.9 (30.8); H, 6.25 (6.17); N, 15.45 (15.17); Ni, 10.80 (10.60).

The nickel(II) complex may be oxidized readily to nickel(III) by using aquacobalt(III) in acidic media or NO^+ in aprotic (CH_3CN) solvents.

A convenient synthesis of the nickel(III) complex was achieved by oxidation with 3.50 M HNO_3. To [Ni((*R*)-Me-9-aneN_3)$_2$](ClO_4)$_2$ (400 mg) was added 0.5 mL of 3.50 M nitric acid. After a few seconds the solution turned from purple to a deep yellow-green color, and within minutes precipitation of the brownish green Ni(III) species commenced. When the solution was allowed to stand overnight at 0 °C, the yield of the nitrate salt was essentially quantitative.

Cyclic voltammograms were obtained by using a Princeton Applied Research Model 273 with Pt electrodes. Over the range 0.1–1.1 V in 1.0 M HNO_3 or 0.9 M $LiNO_3$/0.1 M HNO_3 solutions, a single wave was observed at 0.94 V (vs NHE) that showed near reversibility (70-mV peak–peak separation). This is very close to that noted for the corresponding (9-aneN_3)$_2$ complex (0.95 V).[22] The nickel(III) species is quite stable in aqueous solutions below pH 3 and indefinitely stable in acetonitrile.

Electron spin resonance spectra of the nickel(III) species were measured in frozen (77 K) matrices by using a Varian E6 spectrometer. *g* values were measured by using DPPH ($g = 2.0037$) as an internal standard. Solutions prepared with the nickel(III) complex showed quasi-axial symmetry with evidence for hyperfine splitting of the $g_\parallel$ feature due to the axially coordinated nitrogen donors (Figure 1).

Of interest is the effect of ionic strength on the ESR spectrum, which may be related to outer-sphere ion pairing with anions. From the solid Ni(III) complex (nitrate salt) was prepared a solution in deionized water that was frozen immediately. This showed an isotropic spectrum ($g_{iso} = 2.0949$) at 77 K (Figure 1a). On addition of $LiNO_3$ to yield a NO_3^- concentration of 0.1 M, departure was observed toward a pseudoaxial spectrum. Addition of further nitrate (as HNO_3) provided evidence at 1.5 and 3 M concentrations (Figure 1c) of the complete separation of the $g_\parallel$ and $g_\perp$ features to give an axial spectrum with hyperfine interactions observed in the parallel signal. The intermediate (0.1 M) spectrum may be interpreted as deriving from an equilibrium mixture of the isotropic and axial spectra associated with the free cation and the ion-paired species. Outer-sphere association causes an asymmetry that produces the separation of the *g* values. This finding is important in considering the reduction by iodide ion where a preequilibrium is postulated prior to the electron transfer.

UV-visible spectra of $Ni^{II}L_2^{2+}$ show the following features [λ, nm (ε, L mol^{-1} cm^{-1})]: 310 (74.8), 500 (5.0), 798 (11.3).

For the nickel(III) complex the corresponding values are as follows: 274 (7.3 × 10^3), 315 (7.86 × 10^3), 795 (112).

The stopped-flow and data acquisition systems have been described previously.[29] Absorbance data were collected and processed by an IBM PC microcomputer interfaced to the spectrophotometer via a Techmar Inc. PC-Mate Lab Master Module. Nickel(III) complexes were prepared in situ by oxidation of the corresponding nickel(II) ions using a stoichiometric deficiency of Co^{3+}(aq). Ionic strength was maintained constant at 1.0 M by using mixtures of either $HClO_4$/$LiClO_4$ or HNO_3/$LiNO_3$ depending on solubility of the complex. Reactions were monitored over the range 360–600 nm. Experiments were carried out using pseudo-first-order conditions (10-fold excess of reductant), and rate constants were derived from least-squares plots that were linear for more than 3 half-lives. Where free energy changes are quite small ($\Delta E \sim 0.1$ V), some reversibility is observed. In these circumstances, e.g. in conditions of excess of [Ni^{II}cyclam^{2+}] and [Ni(Me-9-aneN_3)$_2^{2+}$], both the forward and reverse steps of (2) may be treated as pseudo-first-order.

$$\mathrm{Ni(Me\text{-}9\text{-}aneN_3)_2^{3+} + Ni(cyclam)(H_2O)_2^{2+} \rightleftharpoons Ni(Me\text{-}9\text{-}aneN_3)_2^{2+} + Ni(cyclam)(H_2O)_2^{3+}} \quad (2)$$

Results

For all redox reactions studied, the stoichiometry (to +2%) may be represented by a one-electron transfer. No hydrogen ion dependences were observed over the range 0.02–1.0 M H^+, as expected from the lack of any protonation equilibria exhibited by the reactants.

(a) Hydrolysis of the Nickel(II) Complexes. The stability of the Ni^{II}(Me-9-aneN_3)$_2^{2+}$ complex was investigated in acidic media. Kinetic studies were made over the range 0.2–0.9 M. The decomposition is unusually slow for an octahedral nickel(II) species, confirming the thermodynamic stabilization imparted on coordination of the two facial N_3 donor ligands and the establishment of the various chelate rings. Rate studies were carried out (I = 1.0 M) in acidic perchlorate media. The results are presented in the supplementary material (Table Is), where it may be seen that a linear dependence is observed with respect to proton concentration. The observed rate law may be expressed in the form

$$\text{rate} = k_H[\mathrm{Ni(II)}][\mathrm{H^+}] \quad (3)$$

with $k_H = (1.81 \pm 0.09) \times 10^{-4}\ M^{-1}\ s^{-1}$ at 30 °C. Thus, in 1.0 M H^+, the half-life of the nickel(II) complex is 70 min. This may be contrasted[30] with 10 s for the corresponding $Ni(en)_3^{2+}$ ion under comparable conditions. In acidic media any reactions in the stopped-flow time scale show negligible decomposition of the nickel(II) during the course of the experiment. From the rate law it may be inferred that protonation at one of the coordinated secondary amines perturbs the facial configuration of the ligand, leading to relatively easy access of other hydrogen ions to complete the ligand dissociation.

(b) Oxidation of NiL_2^{3+} by Aquacobalt(III). Addition of Co^{3+}(aq) to a nickel(II) solution gives rise to an immediate intense green coloration associated with the nickel(III) ion. Spectrophotometric titration showed a strict 1:1 stoichiometry with an isosbestic point at 224 nm. Kinetic measurements were carried out at λ = 340–360 nm, where the absorbance is attributable solely to the nickel(III). The results are summarized in Table Ia. The rate is strongly hydrogen ion dependent. Pseudo-first-order experiments are consistent with the rate law

$$d[\mathrm{Ni(III)}]/dt = k_2[\mathrm{Ni(II)}][\mathrm{Co(III)}] \quad (4)$$

Since there are no proton-related dependences associated with the reductant, the mechanism may be expressed as (L = Me-9-aneN_3)

$$K_h = [\mathrm{CoOH^{2+}}][\mathrm{H^+}]/[\mathrm{Co^{3+}}]$$

$$\mathrm{NiL_2^{2+} + Co^{3+}(aq) \xrightarrow{k_5} NiL_2^{3+} + Co^{2+}} \quad (5)$$

$$\mathrm{NiL_2^{2+} + CoOH^{2+} \xrightarrow{k_6} NiL_2^{3+} + Co(II)} \quad (6)$$

The overall second-order rate constant may thus be written in the form

$$k_2 = k_5 + k_6K_h/[\mathrm{H^+}] \quad (7)$$

and plots of k_2 against $[H^+]^{-1}$ are linear, leading to $k_5 = 638 \pm 28\ M^{-1}\ s^{-1}$ and $k_6K_h = 251 \pm 7\ s^{-1}$ ($R^2 = 0.992$). In the range $[H^+] = 0.01$–1.0 M, with $K_h \ll [H^+]$ and $K_h = 2 \times 10^{-3}$ M,[31] $k_6 = (1.25 \pm 0.15) \times 10^5$. The rates are broadly similar to those for the reaction of the Ni^{II}(9-aneN_3)$_2^{2+}$ ion ($k_5 = 430\ M^{-1}\ s^{-1}$, $k_6 = 1.35 \times 10^5\ M^{-1}\ s^{-1}$), reflecting almost identical $E°$ values. The rate constant for the hydroxo pathway, k_6, lies in the range 10^5–$10^6\ M^{-1}\ s^{-1}$ derived previously for reactions of this type.

(c) Oxidation of NiL_2^{2+} by Ni^{IV}(oxime). The oxime dianion 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione

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Table I. Kinetic Data for Reactions of $NiL_2^{3+/2+}$

(a) Hydrogen Ion Dependence of the Rate of Oxidation of NiL_2^{2+} by Co(III)
λ = 342 nm, [Ni(II)] = 4 × 10^{-4} M, [Co(III)] = 2.5 × 10^{-5} M, I = 1.5 M

$[H^+]$/M	0.10	0.20	0.25	0.30	0.35	0.40
$k_2/M^{-1}\ s^{-1}$	3144 ± 35	1866 ± 16	1728 ± 19	1476 ± 8	1382 ± 10	1246 ± 10
$[H^+]$/M	0.45	0.50	0.60	0.75	0.80	1.00
$k_2/M^{-1}\ s^{-1}$	1232 ± 8	1090 ± 10	1082 ± 9	942 ± 16	936 ± 18	776 ± 20

(b) Reaction of NiL_2^{2+} with Ni^{IV}(oxime)
$[H^+]$ = 0.5 M, I = 1.0 M (ClO_4^-), T = 25 °C, λ = 500 nm, [Ni(IV)] = 1.9 × 10^{-5} M

10^4[Ni(II)]/M	4.01	8.0	16.01
10^2k_{obsd}/s	1.33	3.20	6.24

mean k_8 = 40.4 ± 2.2 $M^{-1}\ s^{-1}$

(c) Reaction of $Ni^{III}L_2^{3+}$ with $Co(phen)_3^{2+}$
$[H^+]$ = 0.5 M, I = 1.0 M (NO_3^-), T = 25 °C, λ = 360 nm, $[Ni^{III}L_2^{3+}]$ = 1.9 × 10^{-6} M

10^5[Co(II)]/M	4.0	6.0	8.0	14.0
k_{obsd}/s	12.4	19.0	25.9	44.9

mean k_9 = (3.2 ± 0.1) × 10^5 $M^{-1}\ s^{-1}$

(d) Reaction of Iodide with $Ni^{III}L_2^{3+}$
λ = 340 nm, [Ni(III)] = 2 × 10^{-5} M, I = 1.0 M (ClO_4^-), T = 25 °C

$[H^+]$ = 0.02 M

$10^4[I^-]$/M	5	25	100	
$k_2/M^{-1}\ s^{-1}$	210	214	226	mean 213 ± 6

$[H^+]$ = 0.2 M

$10^4[I^-]$/M	5	25	100	
$k_2/M^{-1}\ s^{-1}$	212	206	217	mean 212 ± 4

k_1 = 213 ± 5 $M^{-1}\ s^{-1}$

dioximate(2−) (oxime) has been shown[14,15] to coordinate to nickel ions with deprotonation of the oxime groups in the Ni(IV) state. Previous studies have shown that there is no hydrogen ion dependence on reduction to Ni^{III}(Hoxime) and that the latter species is a strong oxidant that reacts rapidly with a second mole of reductant to give, on protonation, the stable $Ni^{II}(H_2oxime)$ complex. Spectrophotometric titration of $Ni^{II}(Me\text{-}9\text{-}aneN_3)_2^{2+}$ with Ni^{IV}(oxime) showed 2.05 mol of reductant required/mol of Ni(IV). Kinetics studies were made at $[H^+]$ = 0.5 M under conditions of excess reductant. The data presented in Table Ib are consistent with the rate law

$$\text{rate} = k_8[Ni^{II}L_2^{2+}][Ni(IV)] \qquad (8)$$

with k_8 evaluated as 40.4 ± 2.2 $M^{-1}\ s^{-1}$.

(d) Reduction of $Ni^{III}L_2^{3+}$ with $Co(phen)_3^{2+}$. Kinetic studies were carried out in nitrate media to increase solubility of the reductant, which was present in excess. Spectrophotometric data are consistent with (±2%) the one-electron transfer

$$Ni^{III}L_2^{3+} + Co(phen)_3^{2+} \xrightarrow{k_9} Ni^{II}L_2^{2+} + Co(phen)_3^{3+} \qquad (9)$$

There was no observed dependence on $[H^+]$, and studies were made at various Co(II) concentrations in 0.5 M HNO_3. The data (Table Ic) conform to first-order behavior in both reagents. The overall second-order rate constant, k_9 = (3.2 ± 0.05) × 10^5 $M^{-1}\ s^{-1}$, is consistent with an outer-sphere electron transfer.

(e) Oxidation of Iodide by $Ni^{III}L_2^{3+}$. There is a ready oxidation of I^- to I_3^- by the nickel(III) complex:

$$2NiL_3^{3+} + 2I^- \xrightarrow{k_1} 2NiL_2^{2+} + I_2 \quad (I^- \rightarrow I_3^-) \qquad (10)$$

Kinetic studies were carried out at a variety of hydrogen ion concentrations with no observed rate changes. Rate data at 0.02 and 0.2 M $HClO_4$ are presented in Table Id. The dependence on reductant up to 500-fold excess $[I^-]$ is strictly first order. The second-order rate constant k_1 = 214 ± 5 $M^{-1}\ s^{-1}$.

(f) Reaction of Ni((−)-(*R*)-Me-9-aneN$_3$)$_2^{2+}$ with Ni(9-aneN$_3$)$_2^{3+}$. Although the ΔE value for the reaction is 0.005 V, there is still an observable change on mixing of the reagents, enabling rate data to be derived for both the forward and reverse processes. As indicated earlier, for an equilibrium of this type

$$NiL_2^{3+} + NiL'^{2+}_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NiL_2^{2+} + NiL'^{3+}_2 \qquad (11)$$

in conditions of excess of $[NiL'_2]^{2+}$ and $[NiL_2^{2+}]$, the equilibrium may be treated as two pseudo-first-order reactions. The observed first-order rate constant, k_{obsd}, may be expressed in the form

$$k_{obsd} = k_f[NiL'^{2+}_2] + k_b[NiL_2^{2+}] \qquad (12)$$

At constant $[NiL_2^{2+}]$, plots of k_{obsd} against $[NiL'^{2+}_2]$ should be linear. Intercepts of lines of common slope (k_f) should be a linear function of $[NiL_2^{2+}]$ to yield k_b. Experimental data are provided in supplementary material Table IIs. It may be seen from Figure 2 that such is the case, with (eq 11) k_f = (3.15 ± 0.04) × 10^3 $M^{-1}\ s^{-1}$ and k_b = (2.31 ± 0.14) × 10^3 $M^{-1}\ s^{-1}$. The ratio of the rate constants (K = 1.36) is in excellent agreement with the equilibrium constant (K = 1.22) derived from electrochemical data.

(g) Reaction of Ni((−)-(*R*)-Me-9-aneN$_3$)$_2^{2+}$ with Ni(cyclam)$^{3+}$. In view of the similarities in $E°$ values, (ΔE = 0.037 V), the reactions were investigated as outlined above for the equilibrium situation. The data presented in supplementary Table IIs(b) are consistent with k_f = (7.8 ± 0.2) × 10^3 and k_b = (1.60 ± 0.41) × 10^3 M^{-1} s^{-1}, leading to an equilibrium constant K = 4.9. This value is in reasonable agreement with the K = 3.2 calculated from electrochemical measurements.

Discussion

The nickel(III) species formed in either aqueous or nonaqueous medium has an ESR spectrum characteristic of a low-spin d^7 ion. The g values ($g_\parallel$ = 2.031; $g_\perp$ = 2.114; 9.5 GHz) are typical for such an ion, and there is evidence for hyperfine interaction involving the axially coordinated nitrogen donors. ($A_\parallel$ = 18.3 G). In this regard, the ESR spectrum is nearly similar[21,33] to those for the $Ni(9\text{-}aneN_3)_2^{3+}$ ion ($g_\parallel$ = 2.02; $g_\perp$ = 2.14; $A_\parallel$ = 23.7 G) and for the $Ni(bpy)_3^{3+}$ ion, which also show NiN_6 coordination[19] ($g_\parallel$ = 2.02_7; $g_\perp$ = 2.13_7). In aqueous media, the nickel(III) complexes showed considerable stability with little decomposition at pH 3, over a 24-h period. Although the UV–visible spectrum is dominated by a strong charge-transfer band at λ_{max} = 310 nm, there is evidence of a weak d–d absorption at 550 nm and of a further feature at 800 nm (ϵ = 112 $M^{-1}\ cm^{-1}$).

The lack of any $[H^+]$ dependence in the reactions with $Co(phen)_3^{2+}$ and I^- is consistent with the absence of protonation equilibria for Ni(III/II), and substitution inertness of the octahedral $NiN_6^{3+/2+}$ configuration requires an outer-sphere electron transfer. The Marcus theory[32,33] may be used to estimate the

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Table II. Marcus Parameters[a] for the Redox Reactions of NiL_2^{2+} at 25 °C with $E°$(NHE) = 0.940 V for $NiL_2^{3+/2+}$

no.	reactant	$E°$/V	$k_{11}/M^{-1}\ s^{-1}$	K_{12}	$\ln (K_{12}k_{11}f_{12})$	$K_a/M^{-1}\ s^{-1}$
1	$Co(phen)_3^{2+}$	0.37[b]	8[b]	4.51×10^9	21.15	3.2×10^5
2	$Ni(oxime)^{2+}$	0.65[c,d]	6×10^4[d]	1.22×10^{-6}	−1.41	40.4
3	Co^{3+}	1.86[e]	10^{-12}[f]	3.9×10^{15}	3.51	6.4×10^2
4	I^-	1.40[g]	2×10^8[h]	1.61×10^{-8}	2.61	30[i]
5	$Ni(9\text{-}ane)_2^{3+}$	0.947[j]	6×10^3[k]	1.4	9.00	3.15×10^3
6	$Ni(9\text{-}ane)_2^{2+}$[l]	0.947[j]	6×10^3[k]	0.74	8.39	2.31×10^3
7	$Ni(cyclam)^{3+}$	0.97[m]	2×10^3[m]	3.9	8.95	7.8×10^3
8	$Ni(cyclam)^{2+}$	0.97[m]	2×10^3[m]	0.26	6.25	1.60×10^3

[a] See text; k_a = second-order rate constant for reaction. [b] Baker, B. R.; Basolo, F.; Neumann, H. M. *J. Phys. Chem.* **1959**, *63*, 371. [c] Macartney, D. H.; McAuley, A. *Can. J. Chem.* **1983**, *61*, 103. [d] Reference 16. [e] Reference 31. [f] Endicott, J. F.; Durham, B.; Kumar, K. *Inorg. Chem.* **1982**, *21*, 2437. [g] Adedinsewo, C. O.; Adegite, A. *Inorg. Chem.* **1979**, *18*, 3579. [h] Fairbank, M. G.; McAuley, A. *Inorg. Chem.* **1987**, *26*, 2844. [i] Value quoted assumes K_0 ion-pairing constant = 7 M. [j] Reference 22. [k] Reference 21. [l] Reverse reaction of (13). [m] Reference 24.

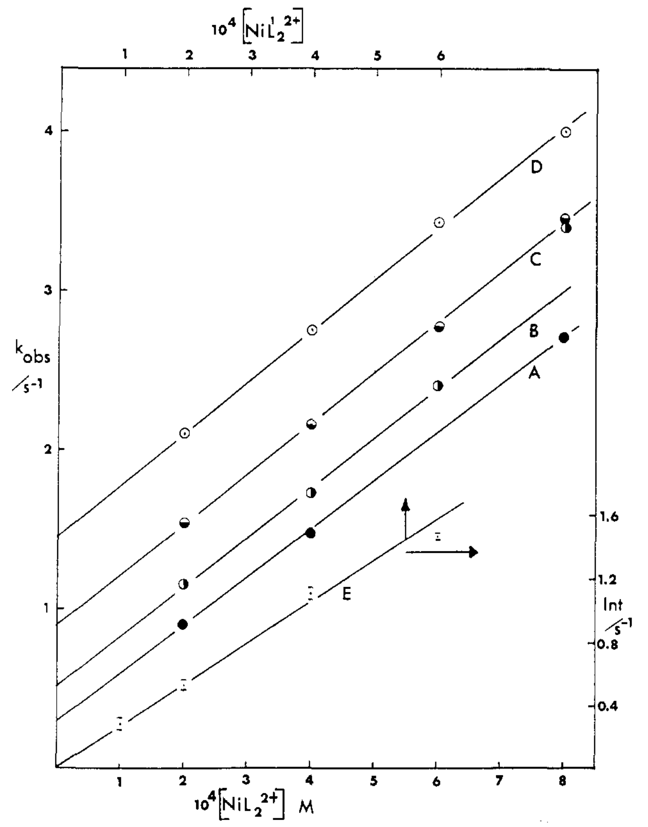

Figure 2. Kinetic data for the reaction of $Ni((-)\text{-}(R)\text{-}Me\text{-}9\text{-}aneN_3)_2^{2+}$ (NiL_2^{2+}) with $Ni(9\text{-}aneN_3)_2^{3+}$ ($NiL'_2{}^{3+}$) ($[H^+]$ = 0.15 M, I = 1.0 M). Reversibility is observed in conformity with eq 13. A–D are plots for 2 × 10^4, 4 × 10^4, 6 × 10^4, and 8 × 10^4 M [NiL_2^{2+}]; slopes = k_f = (3.15 ± 0.4) × 10^3 $M^{-1}\ s^{-1}$. E is a plot of intercepts from A–D versus $[NiL'_2]^{2+}$ (right-hand abscissa and upper ordinate); slope k_b = (2.3 ± 0.4) × 10^3 $M^{-1}\ s^{-1}$.

self-exchange rate for the complex. The second-order rate constant, k_a, for the reactions is related to the individual exchange constants k_{11} and k_{22} and to the overall equilibrium constant, K_{12}, by eq 13. The work terms w_{12} and w_{21} represent the work required

$$k_a = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{13}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln (k_{11}k_{22}/A_{11}A_{22}) + (w_{11} + w_{22})/RT]} \tag{14}$$

$$W_{12} = \exp[w_{12} + w_{12} - w_{11} - w_{22}/2RT] \tag{15}$$

to bring the reactants and the products, respectively, to the separation distance; the sum of the ionic radii, w_{11} and w_{22}, relate to the exchange process. The terms have been described in recent papers from this laboratory.[21] Since, for most systems under consideration, reactants and products are of the same charge, work terms are generally small. Equation 13 may be rewritten as

$$\ln k_a - \ln W_{12} = 0.5 \ln (K_{12}k_{22}f_{12}) + 0.5 \ln k_{11} \tag{16}$$

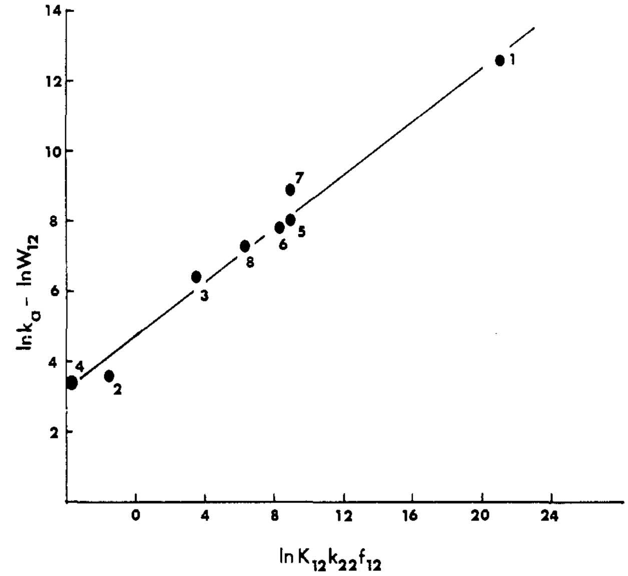

Figure 3. Plot of $\ln k_a - \ln W_{12}$ against $\ln (K_{12}k_{22}f_{12})$ for the Marcus cross-correlation (intercept = 0.5 $\ln k_{11}$). Reactions are identified by number according to Table II. Point 4 (reduction of iodide) is plotted by using preequilibrium constant K_0 = 7 M.

and a plot of $\ln k_a - \ln W_{12}$ against $\ln (K_{12}k_{11}f_{12})$ should be linear with slope 0.5 and intercept 0.5 $\ln k_{11}$. With the data in Table II, the plot (Figure 3) may be obtained. The least-squares slope is 0.38 ± 0.2, and the self-exchange rate of (1.2 ± 0.5) × 10^4 $M^{-1}\ s^{-1}$ is obtained. Of interest is the fact that data from both oxidation and reduction reactions are indistinguishable on the line. The value for the slope is somewhat lower than that expected from the Marcus treatment. This has been encountered previously in similar systems.[21] In the case of the iodide reaction, a preequilibrium constant, K_0 = 7 M^{-1}, for the formation of the (NiL_2^{3+},I^-) ion pair has been used to obtain the rate constant k_a in the expression $k_2 = k_aK_0$.

For redox couples involving transition-metal ions, the wide variation in rates of self-exchange has been interpreted, in part, in terms of the reorganization of the inner coordination shells of the reactants. In the case of the Ni(II/III) reactions, there is a transfer of a dσ^* electron between the (d^8) high-spin $Ni^{II}L_2^{2+}$ and the (d^7) low-spin $Ni^{III}L_2^{3+}$. Attempts have been made recently to describe redox reactivity in terms of M–N bond length changes,[26,34] but few data are available for the Ni(II/III) systems where structural information may be compared with kinetic parameters. In the case[23] of $Ni(9\text{-}aneN_3)_2^{3+}$, the species exhibits

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(33) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.

(34) Brunschwig, B.; Creutz, C.; Macartney, D. H.; Sham, T. K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

Jahn–Teller distortion with the axial bonds 0.139 Å longer than the equatorial. Also, the axial bonds are 0.01 Å longer than than those of the $Ni(9\text{-aneN}_3)_2^{2+}$, whereas the equatorial bonds are 0.129 Å shorter in the Ni(III) species. The self-exchange rate constant for the bis(nonane) system (6×10^3 M^{-1} s^{-1}) is similar to that found in this study. For the *trans*-$Ni(cyclam)Cl_2^{+/0}$ exchange ($k = 3.4 \times 10^4$ M^{-1} s^{-1})[35] the corresponding changes are Δd(Ni–Cl) = 0.04 Å and Δd(Ni–N) = 0.088 Å. If the electron is removed from the $d_{x^2-y^2}$ orbital, then contraction in the equatorial plane will be a factor, and the smaller changes in the dichloro complex may contribute to a more rapid exchange. Clearly, more data are required for a full analysis of these d^8/d^7 reactions. However, methyls, which should hinder ligand rearrangement and perturb the cavity about the metal ion through H–H repulsions, make only slight differences in self-exchange rates. The imposition of greater structural rearrangement, possibly through the use of pendant-arm macrocycles,[36] may be required to provide the sort of bond length difference discrimination and, hence, rate variations observed in other systems.[26] Studies are under way to investigate these aspects.

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Registry No. (*R*)-Me-9-ane, 112816-31-6; $[Ni(Me\text{-}9\text{-aneN}_3)_2](ClO_4)_2$, 68011-41-6; Ni^{IV}(oxime), 55188-33-5; $Co(phen)_3^{2+}$, 16788-34-4; I_2, 20461-54-5; $Ni(9\text{-ane N}_3)_2^{3+}$, 86709-81-1; $Ni(cyclam)^{3+}$, 66199-97-1; (*R*)-$NH_2CH(CH_3)CH_2NH_2$, 6852-78-4; (*R*)-$TsNHCH(CH_3)CH_2NHTs$, 112816-32-7; (*R*)-$TsNCH(CH_3)CH_2NHTs^-$, 112816-33-8; $TsOCH_2CH_2N(Ts)CH_2CH_2OTs$, 16695-22-0; (*R*)-$TsNHCH_2CH(CH_3)N(Ts)CH_2CH_2N(Ts)CH_2CH_2OTs$, 112816-34-9; NaH, 7646-69-7; (*R*)-$Ts\overline{NCH(CH_3)CH_2N(Ts)CH_2CH_2N(Ts)CH_2C}H_2$, 112816-35-0; $[Ni(Me\text{-}9\text{-aneN}_3)_2](NO_3)_3$, 112816-37-2.

Supplementary Material Available: Table Is, listing rates of hydrolysis of $Ni((-)\text{-}(R)\text{-Me-9-aneN}_3)_2^{2+}$ in acidic media, Table IIs, listing rate data for the reactions of $Ni((-)\text{-}(R)\text{-Me-9-aneN}_3)_2^{2+}$ with $Ni(9\text{-aneN}_3)_2^{3+}$ and $Ni(cyclam)^{3+}$, and Figure 1s, showing a plot of k_2 versus $[H^+]^{-1}$ for the reaction of $Ni((-)\text{-}(R)\text{-Me-9-aneN}_3)_2^{2+}$ with Co^{3+}(aq) (4 pages). Ordering information is given on any current masthead page.

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Crown Thioether Chemistry: Homoleptic Hexakis(thioether) Complexes of Nickel(II)

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The Ni(II) complexes of 1,4,7,10,13,16-hexathiacyclooctadecane (18S6, hexathia-18-crown-6), 2,5,8-trithianonane, 1,5,9-trithiacyclododecane (12S3, trithia-12-crown-3), and 1,5,9,13,17,21-hexathiacyclotetracosane (24S6, hexathia-24-crown-6) have been synthesized and characterized by single-crystal X-ray diffraction and electronic spectroscopy. Each of these complexes contains a high-spin $[Ni(thioether)_6]^{2+}$ cation with octahedral microsymmetry. Comparison of these complexes shows that within a conserved coordination sphere the different ring sizes (1) change the Ni–S distances by up to 0.05 Å, (2) affect the ligand field splitting by up to 10%, and (3) greatly influence the stability of the resulting complexes. Crystallographic data: $[Ni(18S6)](picrate)_2$, $C_{24}H_{28}N_6O_{14}S_6Ni$, monoclinic, space group *C*2/*c* (No. 15), $a = 21.079$ (6) Å, $b = 8.685$ (2) Å, $c = 18.399$ (5) Å, $\beta = 93.63$ (2)°, $Z = 4$; $[Ni(12S3)_2](BF_4)_2$, $C_{18}H_{36}B_2F_8S_6Ni$, orthorhombic, space group *Pbca* (No. 61), $a = 19.369$ (9) Å, $b = 12.500$ (5) Å, $c = 11.862$ (2) Å, $Z = 4$; $[Ni(24S6)](BF_4)_2$, $C_{18}H_{36}B_2F_8S_6Ni$, monoclinic, space group *C*2/*c* (No. 15), $a = 13.744$ (5) Å, $b = 17.021$ (5) Å, $c = 13.801$ (5) Å, $\beta = 113.25$ (3)°, $Z = 4$.

Introduction

The electronic consequences of thioether coordination has been a recurring theme in research on the blue copper proteins. Such consequences are best assessed in the context of a homoleptic thioether coordination sphere. Until recently, however, few homoleptic thioether complexes were known; simple dialkyl thioethers often do not bind strongly enough to yield isolable tetrakis- or hexakis(thioether) complexes.[1]

Crown thioethers provide a general solution to this problem. Recent synthetic improvements[2,3] have made readily available a range of ligands (Figure 1)[4] capable of enforcing hexakis(thioether) coordination. Accordingly, their use has recently yielded the first examples of hexakis(thioether) complexes of a number of transition metal ions.[5]

Recent work has also shown that in many cases crown thioether coordination confers unusual electronic structures on a transition-metal ion.[5] For example, $[Rh(9S3)_2]^{3+}$ undergoes reduction to the Rh(I) complex by way of a rare example of a monomeric Rh(II) species.[6,7]

Such unusual behavior inevitably raises the question of whether it arises from the hexakis(thioether) coordination sphere or from a specific effect of the crown ligand. It also raises another question: to what extent can molecular and electronic structure be tuned by geometric deformation of a conserved homoleptic coordination sphere? Ultimately this type of tuning may play a critical role in control of reactivity or specificity of catalytic action.

Several factors make Ni(II) an ideal choice for investigation of these issues. Historically Ni(II) has played a prominent role in the development of coordination chemistry. This is particularly true in the case of macrocyclic thioethers, first studied in the seminal work of Rosen and Busch[8,9] and of Black and McLean.[10,11]

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(4) Abbreviations used: 9S3, 1,4,7-trithiacyclononane (trithia-9-crown-3); 12S4, 1,4,7,10-tetrathiacyclododecane (tetrathia-12-crown-4); 14S4, 1,4,8,11-tetrathiacyclotetradecane (tetrathia-14-crown-4); 15S5, 1,4,7,10,13-pentathiacyclopentadecane (pentathia-15-crown-5); 18S6, 1,4,7,10,13,16-hexathiacyclooctadecane (hexathia-18-crown-6); 24S6, 1,5,9,13,17,21-hexathiacyclotetracosane (hexathia-24-crown-6); ttn, 2,5,8-trithianonane; pic, picrate.

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