

duction of a new range of deoxyaminocyclitol antibiotics.

All the substances described here have been characterized either by elemental analysis or physicochemical methods, especially proton and ^{13}C magnetic resonance.

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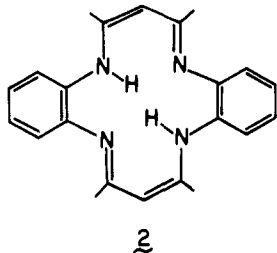
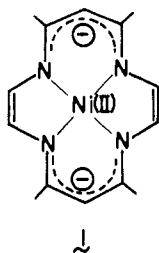
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Electrochemical Generation of a Dimeric Macrocylic Complex

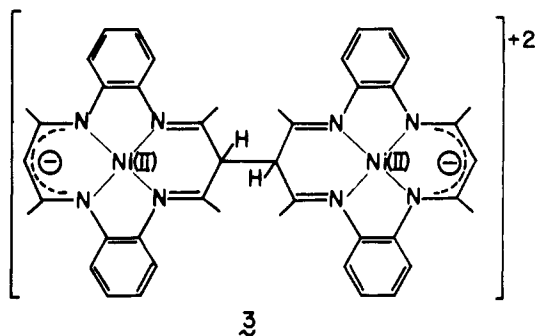
Sir:

The redox properties of synthetic macrocyclic complexes have attracted considerable interest.¹⁻⁴ It has been suggested that certain metal complexes containing antiaromatic tetraazamacrocyclic ligands ($4n\pi$) can be oxidized to the corresponding tetraazaanaluene compounds ($4n + 2, \pi$).⁴ Although the aromatic structures have not yet been isolated and characterized, a number of physical techniques, primarily ESR, have shown that in the case of **1** (16π) the first oxidation process yields the π cation radical complex $[\text{Ni}^{\text{II}}\text{L}]^+$ (15π).^{4,5} This complex actually exists in a dimer-monomer equilibrium with the dimer containing a Ni-Ni bond.⁶ The compound also exhibits a second oxidation which presumably leads to the formation of the aromatic structure $[\text{Ni}^{\text{II}}\text{L}]^{2+}$ (14π). In the process of exploring the electrochemistry of some manganese(III) complexes containing the antiaromatic structure

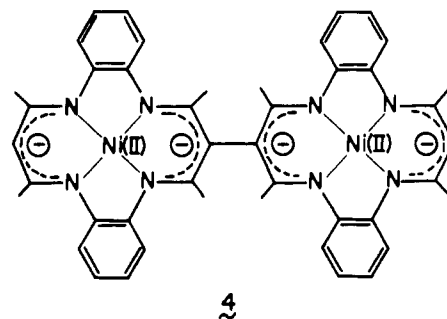


(24π), $\text{H}_2[14]12\text{eneN}_4$, **2**,^{7,8} we investigated the oxidation behavior of $\text{Ni}^{\text{II}}[14]12\text{eneN}_4$. Electrochemical oxidation of $\text{Ni}^{\text{II}}[14]12\text{eneN}_4$ results in the formation of a dimeric com-

plex composed of two macrocyclic units joined via a carbon-carbon single bond bridge, **3**.



The dimer is sensitive to bases and can be readily deprotonated to give **4**. Thus, in this case, the net effect of the electrochemical oxidation has been the joining of two macrocyclic structures via a radical mechanism to give a hindered biphenyl type macrocyclic dimer, **4**. Although both **1** and the nickel complex of **2** initially sustain a ligand oxidation, the distorted saddle shape of the later⁹ apparently leads to the localization of the radical and ultimately radical dimerization via the organic framework. Thus, the attainment of the aromatic structure (in this case 22π) for this type of square planar macrocyclic complex appears to have a hitherto unrecognized structural dependency. This report treats the synthesis and characterization of **3** and **4** as well as the unusual conformational behavior of the protonated dimer, **3**, in solution.



Constant potential electrolysis of $\text{Ni}^{\text{II}}[14]12\text{eneN}_4$ in acetonitrile solution containing either 0.1 N Et_4NBF_4 , $(n\text{-Bu})_4\text{NPF}_6$, or $(n\text{-Bu})_4\text{NSO}_3\text{CF}_3$ as a supporting electrolyte at 0.65 V¹⁰ yielded the dark green moisture sensitive cation, **3**.¹¹ A plot of equivalent conductance Λ_c vs. $c^{1/2}$ for **3** as the BF_4^- salt in the concentration range 9.32×10^{-5} to 4.65×10^{-3} M was linear ($\Delta_0 = 178 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$).¹² The observed and calculated slopes for Et_4NBF_4 and the complex were 345 (obsd) 373 (calcd) and 606 (obsd) 701 (calcd), respectively. The conductance data and electrochemical n values (0.93-0.97) taken with the analytical results indicate that **3** is a 1:2 electrolyte and must thus be composed of two oxidized $\text{Ni}^{\text{II}}[14]12\text{eneN}_4$ units.

Detailed electrochemical studies show that the dimerization process is rapid. If the $0 \rightarrow +1$ couple is studied using cyclic voltammetry, the peak to peak separation is large, ~ 850 mV, and scan rate dependent. However, in-phase ac polarography shows this process to be electrochemically reversible with an $E_{1/2}$ of 0.43 V and a peak width at half height of 92 mV. Carrying out the redox process at 30 Hz does not allow the π -cation radical which is initially formed to dimerize before it is electrochemically reduced.

The proposed structure of the dimer is supported by IR and ^1H NMR data. The IR spectrum of the complex shows strong bands at 1635 and 1528 cm^{-1} (Nujol mull) which are associated with the isolated imine and diiminate framework of **3**, respectively. However, the most useful structural data can be

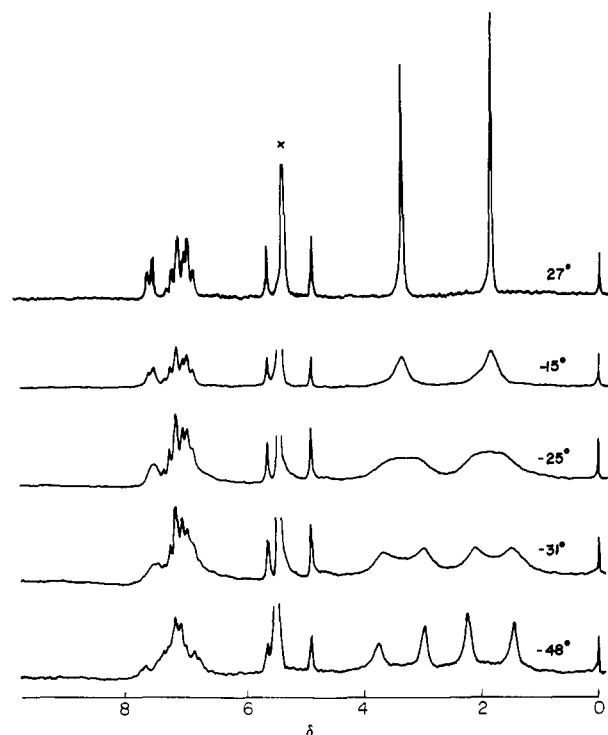


Figure 1. The variable temperature ^1H -FT NMR spectrum of **3** (SO_3CF_3)₂ in CD_2Cl_2 . All shifts in the text are reported relative to Me_4Si . The relatively broad lines observed at low temperature are probably due to a longer rotational correlation time.

derived from the ^1H NMR spectra of **3** in CD_2Cl_2 solution (Figure 1). At 27°C the $^- \text{SO}_3\text{CF}_3$ salt of **3** exhibits two singlets at δ 1.80 (12 H) and 3.33 (12 H) which are assigned to the methyl groups attached to the diiminate and isolated imine chelate rings, respectively. The singlets at δ 4.81 (2 H) and 5.58 (2 H) are associated with the olefinic protons and the two protons attached to the bridging carbon atoms, respectively. The assignment of the higher field resonance to the olefinic proton is consistent with that made for **1**⁴ as well as for the $\text{Zn}(\text{II})$ ⁷ and $\text{Ni}(\text{II})$ complexes of **2**. The aromatic protons produce a complicated series of resonances at δ 6.7–7.6 (16 H). Figure 1 also shows that the ^1H NMR spectrum of **3** is temperature dependent. At -48°C the two methyl resonances split into four absorptions of approximately equal intensity, while the resonance at δ 4.81 and 5.58 are unaffected by temperature.

The variable temperature NMR results can be explained by considering the detailed stereochemistry of the dimer. Goedken and co-workers⁹ have shown that the interactions between the methyl groups and the *o*-phenylene protons of **2** and its metal complexes are substantial. All of the compounds studied to date with this ligand are saddle shaped having the *o*-phenylene rings and diiminate framework displaced in opposite directions from the donor plane of the macrocyclic ligand. Molecular models show that conversion of the coordinated cycle to the isolated imine form (e.g., protonation or, in this case, dimerization) should not significantly alter its saddle-shaped appearance. On this basis three isomers are possible for the dimer **3** (Figure 2). Since the carbon-carbon bond can be either axially or equatorially disposed relative to the monomer units, the isomers are designated ax-ax (C_2h), eq-eq (C_2h), and ax-eq (C_s). Molecular models further indicate that the ax-eq isomer experiences strong steric interactions between the monomeric units making it less stable than the other two. The relatively simple low temperature NMR spectrum observed for the system taken with the steric effects experienced by the C_s isomer leads us to conclude that the dimer is rapidly interconverting between the C_2h isomers, eq-eq and ax-ax,

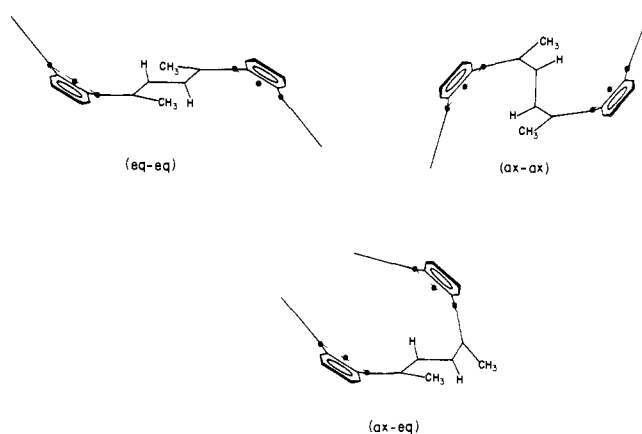


Figure 2. The possible isomers of the cationic dimer **3**. The perspective is in the plane containing the nickel atom and the four nitrogen donor atoms.

at room temperature. Lowering the temperature forces the molecules to collect into two potential wells which from NMR integration have about the same relative energy. Since conversion between the ax-ax and eq-eq isomers can only proceed if the *o*-phenylene moieties are allowed to pass by the methyl groups, the dimer offers a rare look at the "breathing" motion of this macrocyclic structure.

Addition of Et_3N to an acetonitrile solution of **3** leads to the formation of the sparingly soluble dimer **4**. IR (mull) 1528 cm^{-1} , diiminate; ^1H NMR (C_6D_6) δ 1.71 (12 H), 1.86 (12 H), 4.59 (2 H), 6.52 (16 H). Attempted oxidation of **3** and **4** by electrolysis yielded small amounts of highly insoluble materials which coated the working electrode. Although these products could not be characterized their insolubility suggests that they are polymeric rather than further oxidized forms of the dimers.¹³

It is clear from this work that the general oxidation behavior earlier suggested for this class of macrocyclic structure⁴ must be approached with caution. By examining the redox properties of this type of complex as a function of metal and ligand structure, factors affecting the formation of the aromatic compound can hopefully be delineated.

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