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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

THE Ni(II) COMPLEX OF 5,7,12,14-TETRAMETHYLDIBENZO [B,I][1,4,8,11]-TETRAAZA[14]ANNULENE: THE ELECTROPOLYMERIZATION MECHANISM REVISITED

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To cite this Article Hochgesang, Paul J., Bereman, Robert D. and Purrington, Suzanne T. (1995) 'THE Ni(II) COMPLEX OF 5,7,12,14-TETRAMETHYLDIBENZO [B,I][1,4,8,11]-TETRAAZA[14]ANNULENE: THE ELECTROPOLYMERIZATION MECHANISM REVISITED', *Journal of Coordination Chemistry*, 36: 1, 57 – 62

To link to this Article: DOI: 10.1080/00958979508022220

URL: <http://dx.doi.org/10.1080/00958979508022220>

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THE Ni(II) COMPLEX OF 5,7,12,14-TETRAMETHYLDIBENZO [B,I][1,4,8,11]-TETRAAZA[14]ANNULENE: THE ELECTROPOLYMERIZATION MECHANISM REVISITED

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(Received December 6, 1995; in final form March 23, 1995)

To further understanding of the electropolymerization mechanism observed for the nickel(II) complex of 5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene(NiTMTAA), the reduced complex, nickel(II) 4,5,6,7,11,12,13,14-octahydro-5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]annulane (NiH₈TMTAA) was synthesized. The new complex, unlike the oxidized form, does not polymerize on an electrode surface when oxidized. A synthetic scheme for the new complex is presented. The electrochemistry is compared to NiTMTAA and NiTPTAA (where the methyl groups are replaced by phenyl groups).

KEYWORDS: electropolymerization, nickel(II), annulene

INTRODUCTION

For some time we have been interested in characterization of metal complexes that could be used as biomimics for redox centers in metalloproteins. Over the last several years, we studied the electropolymerization of these biomimics into films on electrode surfaces.^{1–9} We found that electropolymerization of tetraazaannulenes complexes can yield films on electrode surfaces with a variety of metals and these films have electro-catalytic properties.^{3,4,7,8} Furthermore, polymerization of these metal complexes can be sterically blocked.^{6,7,9}

Other laboratories have recently investigated the utility of complexes of 5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza-[14]annulenes(TMTAA) as precursors to similar films^{10–15} (Figure 1a). Deronzier and Marques^{10,11} added benzoyl groups with bromomethyl or pyrrole substituents on the γ and γ' carbons of the diiminate backbone. They were able to form polymer films by reductive

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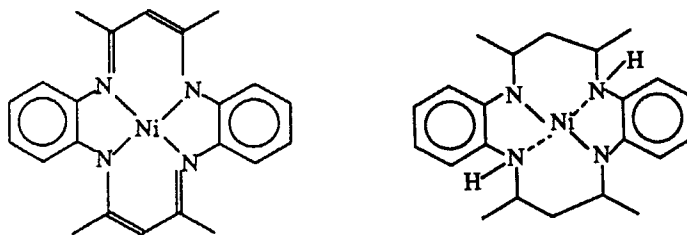


Figure 1 (a) NiTMTAA(a) (b) NiH₈TMTAA(b)

polymerization through these substituents. The metal centers of polymerized complexes were removed and the films were investigated for selective extraction of metal cations. Crayston, *et al.* also investigated annulenes with methyl substituents on the γ and γ' carbons¹² which blocked the polymerization. Lelj, *et al.* investigated how polymerization of [(Co-R) TMTAA] was affected by varying the alkyl group, R, bonded axially to the metal center.¹³ A strong correlation between the alkyl group and the amount of film formed was observed. Ricciardi and Lelj replaced the dibenzo framework of NiTMTAA with a dinaphtho framework and found this new complex also could form films.¹⁴ Furthermore, it formed a bilayer which had rectifying properties with NiTMTAA.

To further elucidate the oxidative polymerization mechanism of nickel(II) 5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene(NiTMTAA) (Figure 1a) we have prepared nickel(II) 4,5,6,7,11,12,13,14-octahydro-5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]-annulene(NiH₈TMTAA). The diiminate backbone in NiH₈TMTAA is fully saturated (Figure 1b). It has been suggested that polymerization of NiTMTAA might be similar to polymerization of ethylene. Oxidation of NiTMTAA results in radical formation. If the polymerization of NiTMTAA is like that of ethylene, these radicals would interact with unsaturated carbons in the diiminate backbone of NiTMTAA. Therefore, if upon oxidation NiH₈TMTAA does not polymerize, it could be inferred that the polymerization of the unsaturated NiTMTAA is similar to that of any olefin. Our results are presented here.

EXPERIMENTAL

Materials

Tetraalkylammonium salts were obtained from Southwestern Analytical Chemicals, Inc., dried overnight at 70°C under vacuum and used without further purification. Aldrich Gold Label acetonitrile and EM Science methylene chloride were dried for 48 hours over 4 Å molecular sieves before use. All other chemicals were obtained from Aldrich Chemical Company.

Synthesis

The complex NiTMTAA was prepared by standard methods^{15,16} outlined in Figure 2. A modification of the procedure of Goedken and Weiss¹⁷ was used for the

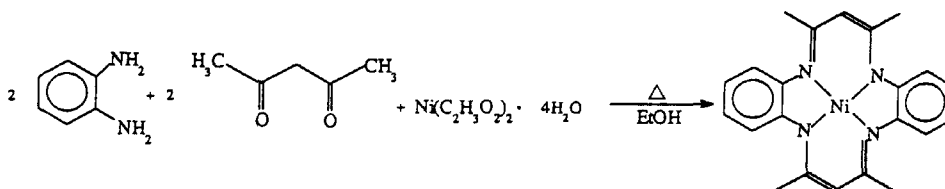


Figure 2 Preparation of NiTMTAA.

demetalization of NiTMTAA as shown in Figure 3. The tetra-pronated macrocycle was treated with ammonium hexafluorophosphate and the complex was reduced with cyanohydridoborate anion.¹⁸ The reduced ligand (H_8 TMTAA) and nickel acetate were mixed in refluxing absolute ethanol for 1 h. The ethanol was removed by vacuum. The resulting solid was dissolved in chloroform and applied to an alumina column. Elution using chloroform yielded a dark blue-green band. Removal of solvent and recrystallization from ethanol followed by vacuum drying for 10 h at 80°C gave the pure product. Melting point (m.p.) 124–126°C, 1H (300MHz, ppm):1.50 (12H, d of q); 1.75 (4H,m); 2.48 (4H,m); 4.30 (2H, d of m); 6.91 (8H, d of m). *Anal. Calc.* for $C_{22}H_{30}N_4Ni$ (%): C, 64.57; H, 7.39; N, 13.69. Found: II C, 64.72; H, 6.94, N, 13.61.

Physical Measurements

Electronic absorption spectra were obtained in methylene chloride solutions using matched 1 cm quartz cells and were recorded with a Cary 2300 Spectrometer. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, Ga.

Electrochemical properties were determined in acetonitrile with 0.1M tetraalkylammonium perchlorate (TEAP) as supporting electrolyte in conventional three compartment H cells. Cyclic voltammograms were obtained using a BAS CV27 potentiostat and recorded with a YEW Model 3022 A4 X-Y recorder. The measurements were made at a Bioanalytical Systems platinum disk electrode. Electrochemical potentials were recorded vs. a saturated calomel electrode. Before use, the disk electrodes were polished sequentially with 3,1 and 0.25 mm diamond

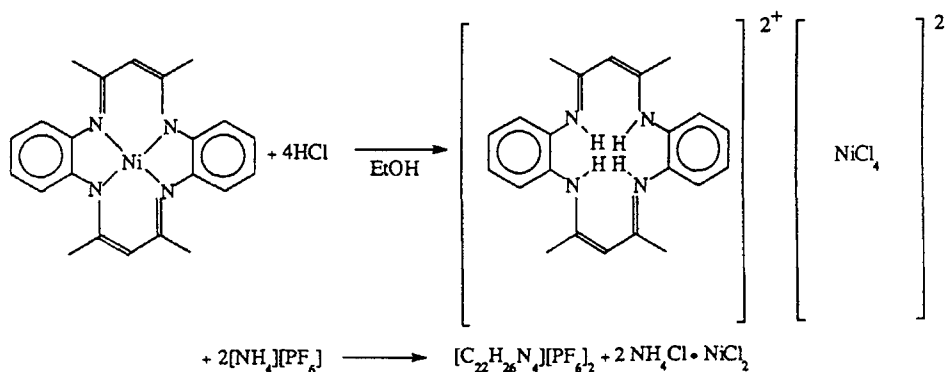


Figure 3 Preparation of the hexafluorophosphate salt.

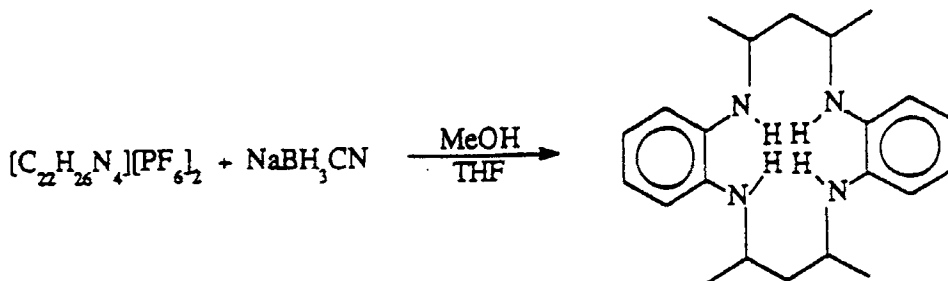


Figure 4 Reduction by sodium cyanohydridoborate to form H_8TMTAA .

paste (Buehler) on a Buehler nylon disk followed by ultrasonic cleaning in deionized water (5 min) and in acetonitrile (gold label) (5 min). When necessary, solutions were degassed for approximately 20 min with argon.

RESULTS AND DISCUSSION

Electronic Spectra

Absorption spectra (examined over the 250–700nm range) for the nickel complexes of the reduced ligand (H_8TMTAA) and the non-reduced ligand (TMTAA)⁵ are compared in Table 1. The NiH_8TMTAA spectrum is red shifted with respect to the NiTMTAA spectrum which implies that the energy between the ground state and the excited state has decreased compared to the non-reduced NiTMTAA complex. The three highest energy electronic transitions are assigned to intraligand electronic transitions.³ These transitions appear to be red shifted to a lesser degree than the fourth electronic transition. The absorptions at 650 and 584 nm are indicative of charge transfer transitions which have been attributed to ligand to metal charge transfer.

Table 1 Electronic absorption bands for NiTMTAA ⁵ and NiH_8TMTAA ^a

Complex	Wavelength(nm)	$E \times 10^{-4}$	$(\text{cm}^{-1}\text{M}^{-1}) (\log t)$
NiTMTAA	584	0.600	(3.78)
	391	1.80	(4.26)
	334	0.732	(3.86)
	266	2.98	(4.47)
NiH_8TMTAA	650	0.349	(3.54)
	431	0.205	(3.31)
	340	0.550	(3.74)
	290	0.750	(3.88)

^aSpectra were obtained for 10^{-4} M solutions in methylene chloride; $T = 22 \pm 2^\circ\text{C}$; wavelength $\pm 0.5\text{nm}$; $E \pm 1\%$.

Table 2 Redox properties of NiH₈TMTAA, NiTMTAA and NiTPTAA^a

Complex	E _{1,2} Ox(1) or Ep ₍₁₎ (V) ^b	E _{1/2} Ox(2) Ep ₍₂₎ (V) ^b	E _{1/2} Red(1)(V) ^b	E _{1/2} Red(2)(V)
NiH ₈ TMTAA	0.13	0.30	-0.94	-1.61
NiTMTAA	0.42	0.97	-1.76	-
NiTPTAA ^c	0.76	1.26	-1.28	-1.73

^a0.1M TEAP acetonitrile solutions; T = 22 ± 2°C. ^bVolts vs. SCE, ± 0.01; sweep rates 200mV/s. ^cNiTPTAA = nickel(II) 5,7,12,14-tetraphenyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene.

Electrochemistry

We have previously shown that solutions of metal complexes of TMTAA form films on electrode surfaces during repetitive cyclic scanning through the oxidation waves of the ligand itself.^{2,5,8} This is easily observed since the area under the curves continues to increase. This continues up to 70 cycles. Recently other laboratories have begun to exploit the polymerizing ability of the tetraazaannulene complexes.^{10,11,13,14} In an effort to further understand the electropolymerization mechanism, we chose to reduce the diiminate backbone of the macrocycle. There are two reversible reductions and two reversible oxidations. The oxidations are moved to lower potential than the non-reversible oxidations of its parent (NiTMTAA) (see Table 2) indicating the complex is oxidized more easily. The oxidation waves of NiH₈TMTAA also span a narrower range with a 17mV separation compared to 55mV for NiTMTAA. NiH₈TMTAA is reduced more easily. Both reduction waves for NiH₈TMTAA occur at more positive potentials than the first reduction wave for NiTMTAA. The electrochemistry of this new complex is rather similar to the nickel macrocyclic complex(nickel(II)5,7,12,14-tetraphenyldibenzo[b,i][1,4,8,11]tetraaza[14] annulene = NiTPTAA) reported earlier.⁶ Both NiH₈TMTAA and NiTPTAA display two reversible oxidation waves and two reversible reduction waves (see Table 2). It is easier to both oxidize and reduce NiH₈TMTAA. As in the comparison of the oxidation waves of NiH₈TMTAA with NiTMTAA, the oxidation waves are closer together for NiH₈TMTAA than for NiTPTAA (17 mV separation vs. 50 mV, respectively). However, the separation between the reduction waves are greater for NiH₈TMTAA than for NiTPTAA. (67 mV separation vs. 45 mV).

CONCLUSION

In contrast to the non-reversible oxidation of NiTMTAA and NiTPTAA, the oxidations for NiH₈TMTAA are reversible. In addition, no dimerization or polymerization is evident since the curves do not show an increase in height. There must be an unsaturated carbon site in the diiminate back-bone for electropolymerization to occur. However, NiH₈TMTAA has no double bonds in the diiminate back-bone and when oxidized to a radical or cation cannot initiate polymerization at an unsaturated carbon site.

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