a mercaptoethanolate ligand and the triply bridging O10. The most unusual feature of the structure is the presence of three distinct ligand geometries for the mercaptoethanolate groups: two terminal chelating, two doubly bridging through both the sulfur and oxygen donors, and one with a terminal sulfur donor and a doubly bridging oxygen donor. Further treatment of II with acid or recrystallization from wet methanol yields the binuclear species $(NBu_4)_4[Mo_2O_2(SCH_2CH_2O_3)(SCH_2CH_2OH)]$.[23]

The characterization of complexes I and II further demonstrates the ability of polyoxomolybdates to undergo chemical transformations characteristic of metal–ligand coordination chemistry[1] and suggests a rich and previously unsuspected molybdenum–oxo–thiolate cluster chemistry.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE 8514634).

Supplementary Material Available: Tables of atomic positions, bond lengths and angles, anisotropic temperature factors, and calculated hydrogen atom positions for I and II (12 pages). Ordering information is given on any current masthead page.

A Novel n-Doped Metallomacrocyclic Conductor

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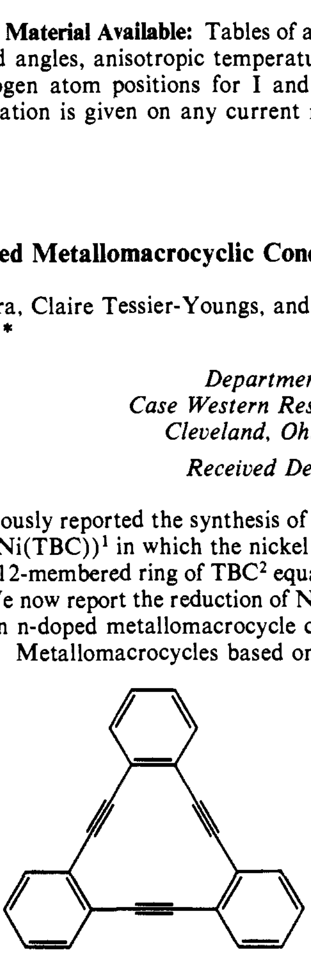
We have previously reported the synthesis of a Ni(0) macrocyclic complex (Ni(TBC))[1] in which the nickel atom resides in the cavity of the 12-membered ring of TBC[2] equally bound to all three alkynes. We now report the reduction of Ni(TBC) and the preparation of an n-doped metallomacrocycle conductor based upon Ni(TBC). Metallomacrocycles based on porphyrin and phthalocyanine type ligands have been studied as precursors for one-dimensional conductors.[3] The ligands of these molecules are planar, have an extended π-system, bind the metal through relatively hard nitrogen atoms, and have a formal negative charge. The resultant metallomacrocycle contains the metal in a positive oxidation state. The properties of Ni(TBC) parallel and contrast those of the nitrogen-based metallomacrocycles. The TBC ligand is also planar and has an extended π-system; however, TBC is neutral and can bind a metal via three soft, polarizable alkyne donors.[1,4] This allows the formation of complexes with a formal zero oxidation state for the metal.



TBC

The slipped stack arrangement of Ni(TBC)[1] is similar to that observed in TTF, TCNQ, and unoxidized Ni(Pc) (Pc = phthalocyanato).[5,3a] Oxidative doping of nickel phthalocyanine results in metal-over-metal stacking.[3a] Experiments on doping Ni(TBC) with iodine give decomposition of the complex yielding TBC and probably NiI_2. The cyclic voltammetry of Ni(TBC) in THF shows two consecutive quasi-reversible waves at strongly reducing potentials which suggests the consecutive formation of a monoanion and a dianion. An oxidizing potential gives decomposition, consistent with the experiments with I_2.[6] The monoanion and the dianion are formed when Ni(TBC) is reduced with lithium, sodium, or potassium. As with the stoichiometric reductions of transition-metal alkene and alkyne complexes,[7] solvated complexes are produced in these solution phase reductions. Without the aid of chelating agents for the alkali metal cation the solids are unstable, especially to dissolution. Several combinations of alkali metals and sequestering agents have been examined. Cryptand-(2.2.2) (C222) with potassium in THF gives the best yields of the dianion.[8] The reduction of Ni(TBC) is sequential. Formation of the red-brown dianion from blue Ni(TBC) occurs via formation of the intermediate purple monoanion. A trace of the monoanion is usually present in the dianion. The alkyne stretching frequency in the IR spectrum decreases from 1983 and 1957 cm^{-1} for Ni(TBC) (C_s symmetry in the solid state) to 1873 and 1834 cm^{-1} for the monoanion and dianion, respectively. The monoanion is EPR active (seven line spectra with $g_{iso} = 2.001$, $a_{iso} = 1.28$ G), consistent with a planar monoanion. The diamagnetic dianion shows an NMR spectrum similar in pattern but slightly shifted downfield from that of Ni(TBC).[1]

By combining Ni(TBC) and $Ni(TBC)^{2-}$ in various ratios n-doped Ni(TBC) has been obtained.[9] A two probe powder conductivity study of the resultant powders gave a conductivity of 2×10^{-3} $(\Omega\text{-cm})^{-1}$ at 0.5 e^-/Ni(TBC) (1:3 ratio of $Ni(TBC)^{2-}$ to Ni(TBC)). A plot of conductivity versus number of electrons per Ni(TBC) is shown in Figure 1. The insulator Ni(TBC) becomes conducting upon partial reduction. Upon further reduction the conductivity again decreases. The results set a lower limit to the conductivity of n-doped Ni(TBC) since measurements by two-probe powder compaction methods typically yield values that are 10^2–10^3 smaller than the corresponding four-probe values.[10] We have examined only a limited number of doping levels and have not determined the ideal doping level. The intensity of the C≡C band for Ni(TBC) decreases monotonically with in-

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[6] Electrochemical and theoretical studies were done in conjunction with Auro Tanaka, Christian Fierro, and Daniel Scherson, manuscript in preparation.

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[8] Reduction of Ni(TBC) with potassium and cryptand(C222): rigorous air sensitive procedures were used throughout.[12] A mixture of Ni(TBC) (2.78×10^{-4} mol), C222 (5.58×10^{-4} mol), potassium (6.90×10^{-4} mol), and THF (70 mL) was stirred for 24 h. The mixture was filtered and concentrated to 3–4 mL. The precipitate was washed with THF and dried in vacuo: yield 0.252 g (76%) of a black-brown solid, $[K(C222)]_2[Ni(TBC)]$; IR (Nujol) 1873 w, 1834 ms.

[9] Doping of Ni(TBC) with $[K(C222)]_2[Ni(TBC)]$: the quantities of Ni(TBC) and $[K(C222)]_2[Ni(TBC)]$ used were calculated based on ~50 mg of doped Ni(TBC). The mixture of solids was dissolved in 20 mL THF and stirred for 10–15 min, and THF was removed in vacuo at room temperature. Each sample was measured for conductivity and an IR (Nujol) spectrum recorded. A control sample of only $[K(C222)]_2[Ni(TBC)]$ indicated slight decomposition when treated as above.

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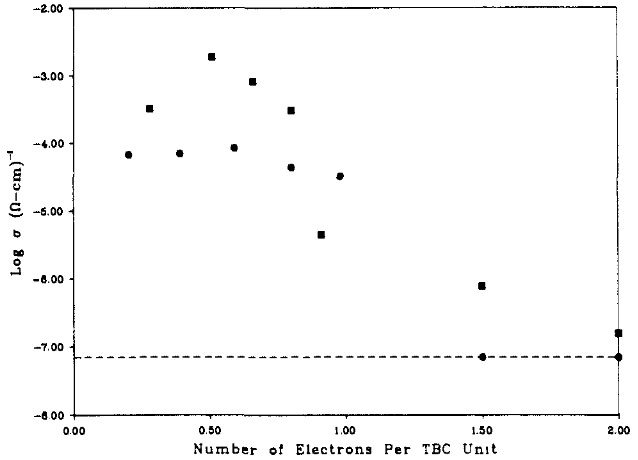

Figure 1. Conductivity versus number of electrons based upon initial stoichiometry for the doping study of Ni(TBC) with $[K(C222)]_2[Ni(TBC)]$ (squares) and TBC with $[K(C222)]_2(TBC)$ (circles). The dashed line represents the lower limit for conductivity measurements with the device used.

creasing proportion of $Ni(TBC)^{2-}$, while the band for $Ni(TBC)^{1-}$ increases. The number of electrons per Ni(TBC) as determined by initial stoichiometry is consistent with the relative amounts of Ni(TBC) and $Ni(TBC)^{1-}$ as determined by IR.

Efforts are currently underway to determine the mechanism of conductivity in Ni(TBC). In particular, two mechanisms of conductivity are under consideration, conductivity via the interacting π-orbitals as in $Ni(Pc)I_x$[3a] or conductivity via the metal spine as in $Co(Pc)I_x$.[3b] Electrochemical, EPR and infrared results, and theoretical calculations[6] indicate the LUMO of Ni(TBC) is primarily ligand centered and antibonding with respect to the alkyne bonds. Ni(0) is a d^{10} species requiring the 4s or 4p orbitals to interact in order to form a conduction band for metal-centered conductivity in this n-doped system. To determine if the nickel was essential to the conductivity in this system a similar study on the free ligand TBC was undertaken.[11] The IR spectrum of reduced TBC shows two bands at 2089 and 2036 cm^{-1} which have been assigned to the monoanion and dianion, respectively. The results of n-doping of TBC show a weak maximum at 0.6 e$^-$/TBC with a conductivity of 8×10^{-5} (Ω-cm)$^{-1}$, 25 times lower than the maximum observed for Ni(TBC). This indicates that while the presence of the nickel atom is not essential for conductivity it does strongly influence the conductivity.

The conductivities of reductively doped Ni(TBC) are comparable to p-doped metallophthalocyanine complexes with the four-probe powder conductivity for $Ni(Pc)(I)_x$ at room temperature being 7.7 (Ω-cm)$^{-1}$.[3a] The conductivities for many other p-doped phthalocyanine complexes lie in this region.[3] The reductive doping of phthalocyanine complexes has been explored recently with room temperature conductivities of $\{K[SiO(Pc)]\}_n$,[3e] $K_2[Co(Pc)]$,[3f] and $K_2[Fe(Pc)]$[3f] of 2×10^{-5}, 5×10^{-3}, and 2×10^{-4} (Ω-cm)$^{-1}$, respectively. These were measured by the four-probe technique.[8] As with the above materials the conductivity of doped Ni(TBC) is expected to be highly anisotropic.

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Registry No. Ni(TBC), 98779-78-3; Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; I_2, 7553-56-2.

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[11] A procedure similar to that in ref 9 was followed for the doping of TBC with $[K(C222)]_2(TBC)$.

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Molecular Recognition: Hydrogen Bonding and Aromatic Stacking Converge To Bind Cytosine Derivatives

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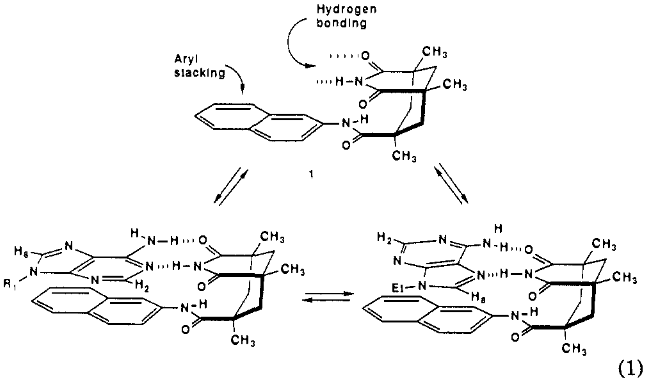
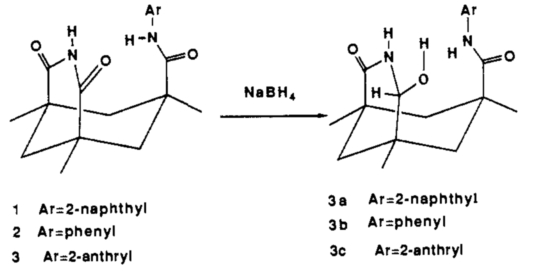
In recent communications from this laboratory we have described model receptors for nucleic acid components.[1] Such structures (eq 1) feature hydrogen bonding and aryl stacking



(1)

surfaces which converge from perpendicular directions to provide a microenvironment complementary to adenine derivatives. Watson–Crick, Hoogsteen, and bifurcated hydrogen bonds are present, and remote structural features influence the subtleties of base-pairing in the recognition event. We now describe modification of these systems that results in their selective binding of cytosine derivatives.

The new molecules are prepared by mere $NaBH_4$ reduction[2] of the imide amides. Specifically, the naphthyl **1**, phenyl **2**, and anthryl **3** derivatives were reduced to give the corresponding hydroxylactam structures **3a–c**. This reaction effectively changes the hydrogen bonding pattern of the imide to a structure complementary to acylated amidines (eq 2). The structures follow



(2)

from spectroscopic features[3] which indicate an intramolecular hydrogen bond between the hydroxyl and the neighboring amide carbonyl. This is revealed by a large coupling constant of the hydroxyl and the α-methine proton (13 Hz) and NOE experiments which indicate that this intramolecular hydrogen bond limits considerably the internal rotations of the structure. The NOE results for **3a** are summarized on the structure. (The proton at

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[3] All new compounds were characterized by a full complement of high-resolution spectra. For **3a** (mp 186–189 °C): ^1H NMR (300 MHz, $CDCl_3$) δ 5.16 (d, J = 13 Hz, 1 H, OH) δ 4.57 (d, J = 13 Hz, 1 H, CH). Similar signals were observed for **3b** (mp 201–204 °C) and for **3c** (mp 223–225 °C).