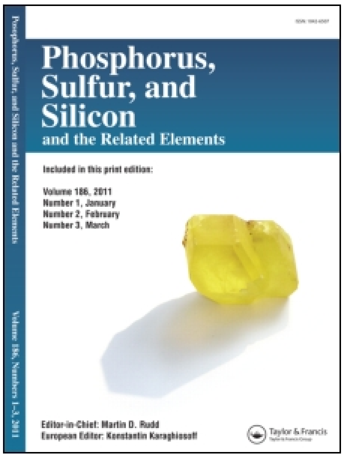

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Synthesis of Dinuclear Thiolate-Bridged Macrocyclic Nickel(II) Complexes with C_2 Linker Diimine

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Macrocyclic dinickel(II) complexes derived from 2,6-diformyl-4-methylthiophenolate and C_2 linking diamine(diaminomalleonitrile ethylenediamine) are prepared and characterized. In these complexes, both metal centers in the N_2S_2 sites are in square-planar configuration and are diamagnetic. The low-spin states of the nickel(II) ions are preserved in polar solvents.

Keywords Cyano group; diamagnetic Ni(II) complex; dinuclear nickel(II) complex; macrocyclic ligand

INTRODUCTION

There have been numerous reports on multinuclear complexes with macrocyclic ligands derived from a condensation reaction of 2,6-diformyl-4-alkylphenol and its counterpart, 2,6-diformyl-4-alkylthiophenolate, with a variety of diamines.[1] However, only a few dinuclear complexes of macrocyclic ligand type **1** incorporating a C_2 linker between the diimine nitrogenes have been known.[2] Atkins et al.[3] and Okawa and Kida[4] have prepared dinuclear Ni(II) complexes of type **1**. The dinuclear complexes obtained contained paramagnetic nickel(II) ions. However, Brooker et al.[5] prepared dinickel macrocyclic complexes with a ligand type **2**, including three carbon atoms (C_3) and higher carbon atoms in the linker between the diimine and diamine. The resultant dinickel macrocyclic complexes exhibited diamagnetic behavior in nonpolar solvents but showed a paramagnetic property in polar solvents.

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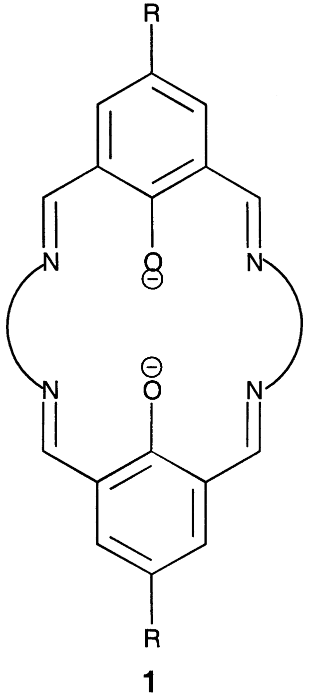
In this study, macrocyclic ligands **2** with a C_2 linker between diimine nitrogen atoms were prepared. It was expected that the modification of an N_4O_2 donor set to N_4S_2 might increase the ligand-field strength of the macrocyclic due to the potential π back-donation and the weaker σ-donor abilities of RS^- compared to RO^-. Also, decreasing the cavity size of the macrocyclic ligand **2** with C_2 linkers might impose a higher ligand field strength and afford a diamagnetic dinickel (II) macrocyclic complex in polar solvents.



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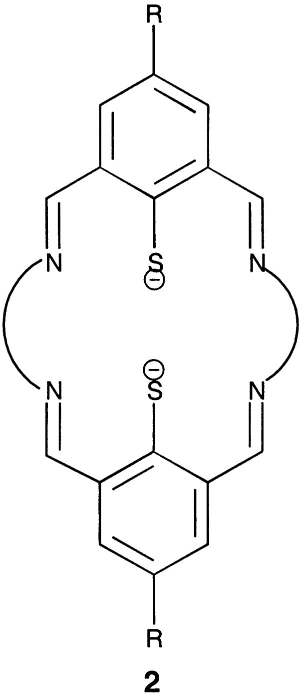

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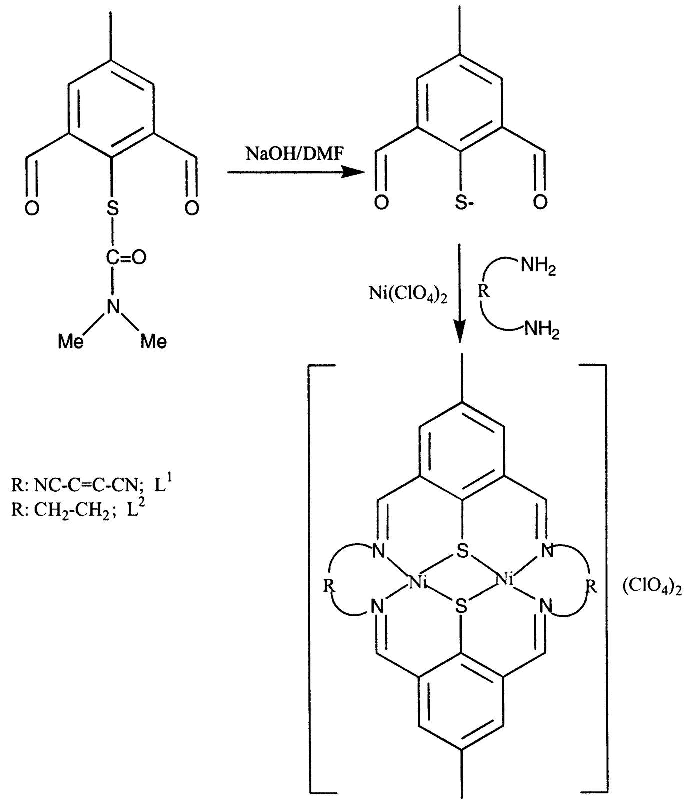
RESULTS AND DISCUSSION

Dinuclear complexes $[Ni_2L^1](ClO_4)_2$ and $[Ni_2L^2](ClO_4)_2$ were obtained in acceptable yield (40%) according to Scheme 1. The 1:1 condensation reaction of 2,6-diformyl-4-methyl thiophenolate (dfmtp) and diamine (diaminomaleonitrile or ethylenediamine) in the presence of nickel (II) ion proceeded to give the dinuclear complexes $[Ni_2L^1]^{2+}$ and $[Ni_2L^2]^{2+}$. The elemental analysis revealed that the metal insertion was sufficient for the 2:2:2 reaction of $Ni(ClO_4)_2$, diamine and



SCHEME 1

dfmtp. These compounds are sparingly soluble in polar solvents at concentrations sufficient for characterization purposes. The IR spectra did not show NH stretching bands or any carbonyl band associated with the diformylthiophenolate starting materials or nonmacrocyclic intermediates. Diaminomaleonitrile itself has one strong $\nu(\mathrm{C}\equiv\mathrm{N})$ stretching frequency at 2210 cm^{-1}, which is replaced in the compound $[\mathrm{Ni_2L^1}](\mathrm{ClO_4})_2$ with two bands, for which one much is stronger than the other, in the same region (2230 (m), 2196 (vw) cm^{-1}).[6] Perchlorate ν_3 and ν_4 modes are seen for both complexes at around 1100 and 625 cm^{-1}, respectively. No splitting of the ν_3 mode means that the Perchlorate group is free from coordination.[7] Strong absorption at 1648 and 1624 cm^{-1} of complexes $[\mathrm{Ni_2L^1}](\mathrm{ClO_4})_2$ and $[\mathrm{Ni_2L^2}](\mathrm{ClO_4})_2$ could be assigned as the stretching band of C=N double band within the ligands, respectively.[4] Both dinuclear complexes were found to be diamagnetic ($\mu = 0.0$ BM in both cases), which is consistent with a square planar nickel(II) formation and the nickel(II) ions being assumed to be low spin states. As expected, both complexes are 2:1 conductors in CH_3CN. UV/Vis spectra of acetonitrile solutions of $[Ni_2L^1](ClO_4)_2$ and $[Ni_2L^2](ClO_4)_2$ exhibit two strong absorption bands at 261 and 388 nm for $[Ni_2L^1](ClO_4)_2$ and 275 and 382 nm for $[Ni_2L^2](ClO_4)_2$, which are assigned to $\pi - \pi^*$ transition of the ligands. One absorption band around 510 nm ($\varepsilon \sim 1200$ L mol^{-1} cm^{-1}) for both compounds is observed, which was assigned as a ligand-to-metal charge transfer transition, $S_\pi \rightarrow Ni$.[8] This band is typical for complexes containing planar NiN_2S_2 units.[9] The spectra taken in polar solvents such as pyridine, dimethylsulfoxide, and acetonitrile are similar to the solid state. That implies that coordination bands in the tetragonal plane are strong enough to exclude the fifth and sixth coordination of the solvent molecules in the axial positions. The ^1H NMR spectra of complexes in CD_3CN indicate diamagnetism. The methylene protons of $[Ni_2L^2](ClO_4)_2$ give rise to resonances at $\delta\,4.30$ ppm, whereas the other proton signals appear almost in the same position as in $[Ni_2L^1](ClO_4)_2$. Attempts to produce X-ray–quality crystals of compounds have been frustrated by the limited solubility of these compounds in suitable solvents and the fact that the macrocyclic ligand L^1 is highly susceptible to reaction with the solvent itself in some cases. Recrystallization of $[Ni_2L^1](ClO_4)_2$ from acetone produced orange-brown crystals, whose infrared spectrum revealed carbonyl stretching bands at 1708 and 1690 cm^{-1}, associated with acetone fragments and the absence of any band associated with ClO_4^-. A preliminary analysis of this compound showed that two acetone molecules have undergone a conjugate addition to two the imine (C=N) linkages to produce saturated C—N groups, with the ligand bearing four negative charges.

SUMMARY

In this study, we successfully prepared new N_4S_2-type macrocycles, which form nearly planar, dinuclear nickel(II) complexes in a such way that two thiolate sulfur atoms in a macrocycle moiety bridge two nickel ions. These macrocyclic ligands impose strong ligand field strength so that nickel ions are in low-spin states and keep their square-planar configurations even in polar solvents such as pyridine owing to the sufficiently strong ligand field. The general low solubility of these complexes has hindered a more extensive spectroscopic and physical characterization. We are presently working on the incorporation of solubilizing groups on ligand backbones and also reducing the diimine moiety of the macrocycle to diamine in the hope of circumventing these solubility problems.

EXPERIMENTAL

Conductance measurements were made at 25°C with a Jenway 400 conductance meter on 1.00×10^{-4} M samples in CH_3CN. Infrared spectra (potassium bromide disk) were recorded using a Bruker FT-IR instrument; only strong peaks are given. The electronic absorption spectra were measured as Nujol mull and solution (with spectral grade solvents) by using a Cecil 5000 model UV-Vis spectrophotometer. Elemental analyses were performed on a LECO 600 CHN elemental analyzer. Absolute metal percentages were determined by atomic absorption-flame spectrometer. ^1H NMR spectra were recorded on a Bruker 500 MHz Fourier transform spectrometer. Electrospray mass studies were conducted on a VG Quattro II (Fision) triple-quadruple electrospray mass spectrometer with methanol and as the mobile phase. The compound was dissolved in a mixture of acetonitrile and methanol (1:1), and the solution was injected directly into the spectrometer via a Rheodyne injector using a Fision LC syringe pump to deliver the solution at a flow rate of 20 $\mu L\,s^{-1}$. Nitrogen was used for nebulization and as a drying gas with flow rates of approximately 20 and 250 $L\,h^{-1}$, respectively. Magnetic susceptibility of powder samples was measured at 20°C using a Johnson Matthey magnetic susceptibility balance. All samples were dried to a constant weight under a high vacuum prior to analysis. S-(2,6-diformyl-4-methylphenol) dimethylthiocarbomate was prepared according to the literature procedure.[10] Isopropanol (IPA) was stored over CaO and then decanted off and distilled. Dimethylformamide (DMF) was distilled from CaH_2 (DMF in vacuo) immediately before use. Acetonitrile that was used was distillated over CaH_2. All other reagents were used as received.

Caution: Perchlorate salts are potentially explosive and should be handled with appropriate care.

$[Ni_2L^1](ClO_4)_2$. S-(2,6-diformyl-4-methylphenol) dimethylthiocarbomate (0.251 g, 1.00 mmol) in IPA (80 mL) was brought to reflux. Then the ground NaOH (0.04 g, 1 mmol) was added to the clear pale yellow solution and caused an instantaneous change to bright orange. The resulting solution was refluxed for 5 h. To this was added $Ni(ClO_4)_2{\cdot}6H_2O$ (0.65 g, 1.00 mmol) in IPA (20 mL) followed by diaminomalleonitrile (0.108 g, 1.00 mmol) in IPA (20 mL). The reaction mixture was refluxed for 4 h and then filtered while hot. The red-brown solid deposited after cooling the dark red solution to the r.t. The product was repeatedly recrystallized from acetonitrile by vapor diffusion of diethyl ether, which yielded a red-brown solid (0.203 g, 40%). UV-Vis (CH_3CN): λ_{max}/nm (ε/L mol^{-1} cm^{-1}) 275 (23200), 362 (16040), 510 (1150); FT-IR (KBr disk) 2940, 2230 (C≡N), 2196 (C≡N), 1648 (C=N), 1612 (C=C), 1450 (aromatic skeleton), 1383, 1104 (ClO_4^-), 625 (ClO_4^-) cm^{-1} ^{1}H NMR (CD_3CN) δ2.26 (s, 6H, Ar-C**H**$_3$), 7.55 (s, 4H, Ar-**H**), 8.63 (s, 4H, Ar-**H**); ESMS *m/z* 615.93 for $\{[NiL^1]^{2+}\text{-}H^+\}^+$ and 308.97 for $[NiL^1]^{2+}$; anal. calcd. for $C_{26}H_{14}N_8O_8S_2Cl_2Ni_2$ (810.90): C, 38.13; H, 1.73; N, 13.69; Ni, 14.33; found: C, 38.44; H, 2.04; N, 13.48; Ni, 14.10; Λ_m (CH_3CN) = 255 mol^{-1} cm$^2\Omega^{-1}$ (c.f. 220–300 mol^{-1} cm$^2\Omega^{-1}$ for a 2:1 electrolyte in CH_3CN); $\mu = 0.0$ BM.

$[Ni_2L^2](ClO_4)_2$. This complex was prepared by a procedure similar to that described for $[Ni_2L^1](ClO_4)_2$ but ethylenediamine was used instead of diaminomalleonitrile. $[Ni_2L^2](ClO_4)_2$ (46%) was obtained as a light brown solid after recrystallization. UV-Vis (CH_3CN): λ_{max}/nm (CH_3CN) (ε/L mol^{-1} cm^{-1}) 261 (40260), 387 (8780), 515 (1200); FT-IR (KBr disk) 2940, 1624 (C=N), 1610 (C=C), 1450 (aromatic skeleton), 1096 (ClO_4^-), 623 (ClO_4^-) cm^{-1}; ^{1}H NMR (CD_3CN) δ2.36(s, 6H, Ar-C**H**$_3$), 4.30 (s, 4H, NC**H**$_2$C**H**$_2$N), 7.37 (s, 4H, Ar-**H**), 9.63 (s, 4H, Ar-**H**); ESMS *m/z* 520.00 for $\{[NiL^2]^{2+}\text{-}H^+\}^+$ and 261.00 for $[NiL^2]^{2+}$; anal. calcd. for $C_{22}H_{22}N_4O_8S_2Cl_2Ni_2$ (722.90): C, 36.32; H, 3.07, N, 7.75; Ni, 16.24. found:C, 36.32; H, 2.80; N, 8.02; N, 16.10; Λ_m (CH_3CN) = 235 mol^{-1} cm$^2\Omega^{-1}$ (c.f. 220-300 mol^{-1} cm$^2\Omega^{-1}$ for a 2:1 electrolyte in CH_3CN); $\mu = 0.0$ BM.

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