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SYNTHESIS AND CHARACTERIZATION OF NICKEL COMPLEX OF 4-AMINO-3-PYRIDINETHIOLATE

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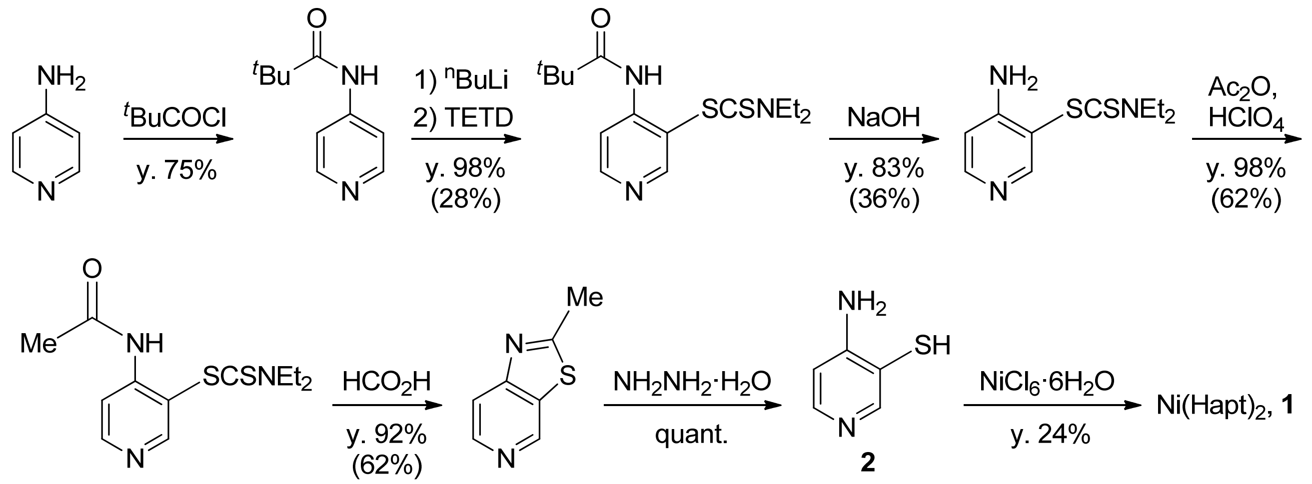
Abstract – A Ni(Hapt)$_2$ complex, apt = 4-amino-3-pyridinethiolate, is isolated and characterized by X-ray crystallography, cyclic voltammetry, and UV-Vis spectroscopy.

The metal complex system M(XYC_6H_4)$_2$ (X, Y = NH, O, S) shows high redox activity[1] and therefore have attracted intense interest as a molecular component of electro-conductive and magnetic materials.[2] The electron transfer reaction of the complexes is a ligand-centered process, which has been judged by ESR studies and quantum chemical calculations.[1] Recent sophisticated DFT calculations applied with the broken-symmetry method demonstrate that the M(XYC_6H_4)$_2$ system possess radical character on the ligands and unpaired electrons are coupled anti-ferromagnetically through the metal center to afford singlet diradical ground state.[3] This peculiar electronic structure may provide third-order non-linear optical properties such as two-photon absorptions to the M(XYC_6H_4)$_2$ system, according to the theoretical work by us.[4] In this way, the ligands in the M(XYC_6H_4)$_2$ system play an important role in their physical properties and new combination of metals and ligands expands the possibility of the M(XYC_6H_4)$_2$ system for functional materials. Herein we report the synthesis and characterization of a new Ni complex (**1**) with ligands of 4-amino-3-pyridinethiolate (apt).

M(XYC_6H_4)$_2$ Ni(Hapt)$_2$, **1**

Figure 1. Metal complex system M(XYC_6H_4)$_2$ and a new Ni complex (**1**)

Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday.



Scheme 1. Synthetic route for **1**. In parentheses, the literature yields[5] are given. TETD = tetraethylthiuram disulfide.

The ligand (**2**) of Ni(Hapt)$_2$ **1** was prepared according to the reported procedure.[5] We found that most of the steps gave much better yields than the reported ones. The ligand **2** was obtained as a colorless solid quantitatively, which gradually changed to oil in air. The reaction of **2** with NiCl$_2$•6H$_2$O in water in a sealed degassed tube at room temperature afforded yellow crystals of **1** suitable for X-ray crystallographic analysis.[6] As will be mentioned below, **1** is subjected to oxidation in a solution state, and therefore, the degassed condition was required for obtaining **1**.

Figure 2 shows the X-ray structure of **1**.[7] There are two crystallographically independent molecules in the unit cell. **1** forms N–H···O hydrogen bonds (N1···O1, 2.955Å; N3···O2, 2.980Å) with water molecules (Figure 2a). Strong bond length alternation is observed in the ligands (Figure 2b), indicating the ground state of **1** can be best described by the chemical structure depicted in Figure 1.

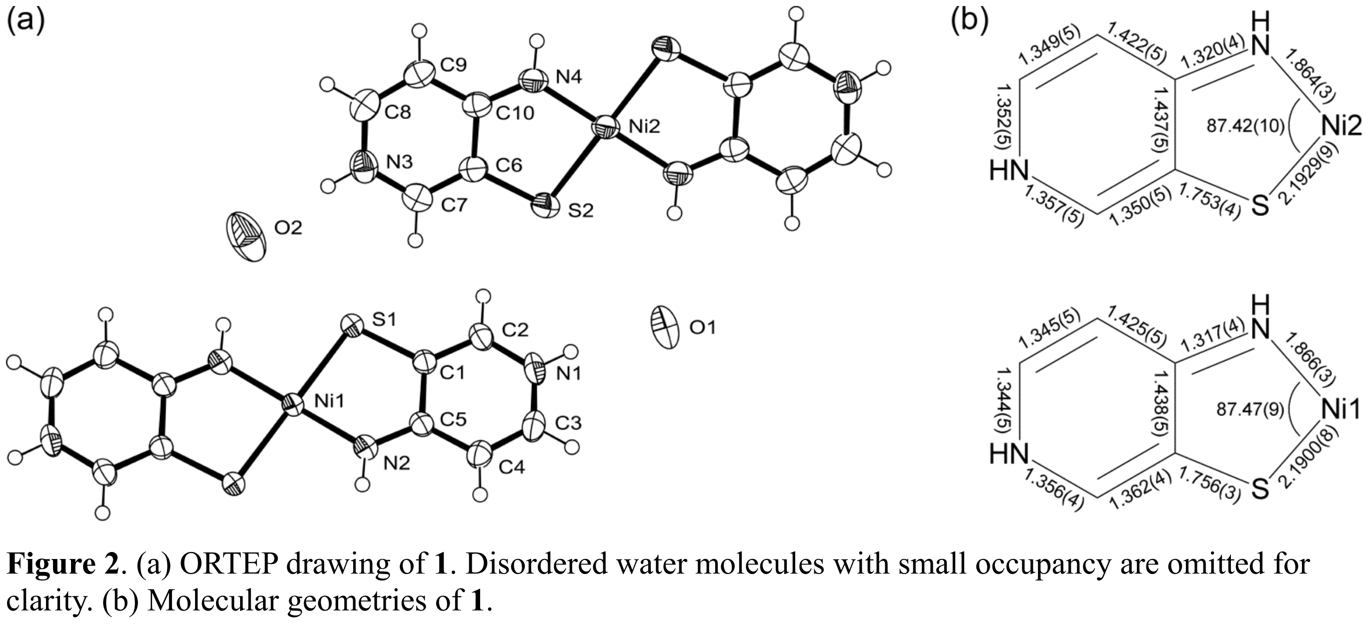


Figure 2. (a) ORTEP drawing of **1**. Disordered water molecules with small occupancy are omitted for clarity. (b) Molecular geometries of **1**.

Cyclic voltammogram (Figure 3a) of **1** gave reversible and irreversible redox waves at –0.40 V ($E_{1/2}$) and +0.12 V (E_{pa}), respectively. The first oxidation potential of –0.40 V is lower than that of tetrathiafulvalene (TTF, $E_{1/2}$ = –0.09 V vs. Fc/Fc$^+$), indicating that **1** has very high electron donor ability. The irreversibility of the second oxidation wave might come from deprotonation at the N-atom of the pyridine ring during the oxidation process. Because the HOMO of **1** is distributed mostly on the ligands, the oxidation is a ligand-centered process. UV-Vis spectrum (Figure 3b) of **1** gave absorption peaks at 407 nm and 272 nm shortly after dissolving in methanol, while after one day the spectrum totally changed to give new peaks at 398 nm and 322 nm, probably due to the oxidation of **1** by air. Unfortunately, the decomposed species could not be identified.

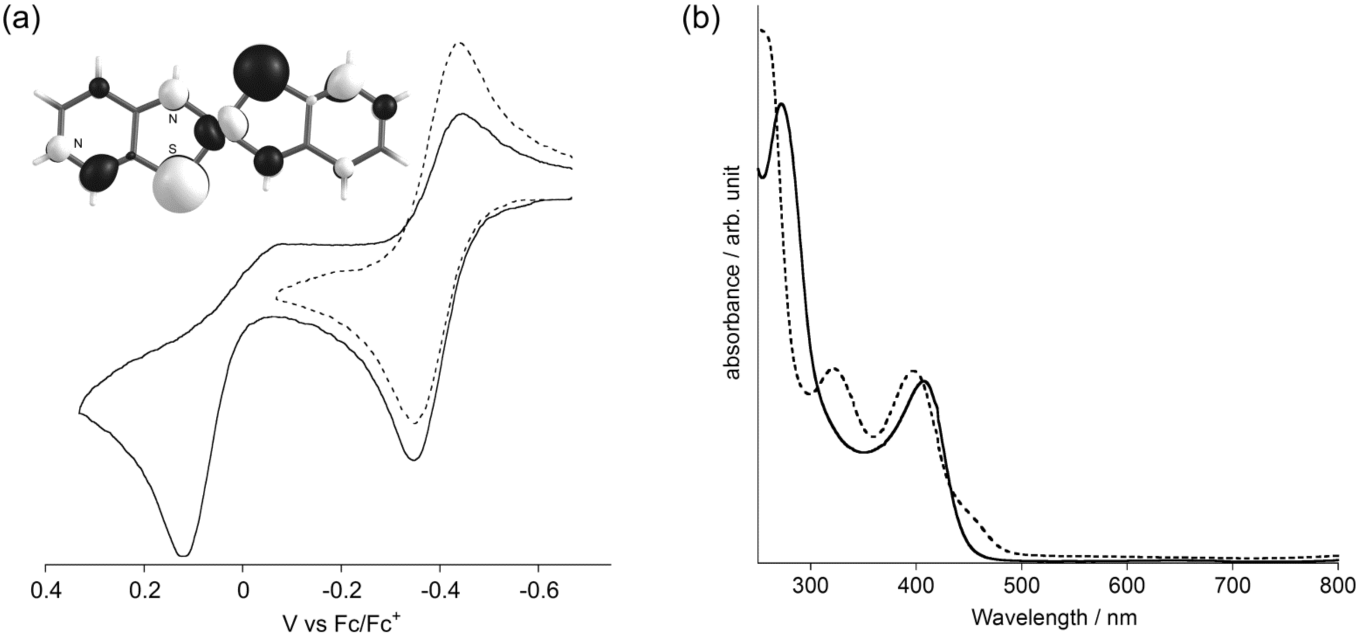


Figure 3. (a) Cyclic voltammogram (solid line, V vs. Fc/Fc$^+$) of **1**. Dashed line is the voltammogram with the scan range of –0.67 to –0.07 V. Measurement conditions; in 0.1M ^{n}Bu$_4$NClO$_4$/DMF, scan rate = 100 mV/s, WE = glassy carbon, CE = Pt, RE = Ag/Ag$^+$, rt. HOMO of **1** is also shown.[8] (b) UV-Vis spectra of **1** (solid line) shortly after dissolving in methanol and (dashed line) after one day.

In summary, we isolated a new Ni complex with ligands of 4-amino-3-pyridinethiolate (apt). The complex, Ni(Hapt)$_2$, was found to possess a high electron donating ability by cyclic voltammetry. Investigation on functional properties of Ni(Hapt)$_2$ such as electro-conductivity and two-photon absorption are now in progress in our group.

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. J. A. McCleverty, 'Progress in Inorganic Chemistry' Vol. 10, ed. by F. A. Cotton, John Wiley & Sons, Inc., New York, 1968, pp. 49–221.
2. N. Robertson and L. Cronin, *Coord. Chem. Rev.*, 2002, **227**, 93.
3. (a) V. Bachler, G. Olbrich, F. Neese, and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 4179; (b) D. Herebian, K. E. Wieghardt, and F. Neese, *J. Am. Chem. Soc.*, 2003, **125**, 10997; (c) T. Petrenko, K. Ray, K. E. Wieghardt, and F. Neese, *J. Am. Chem. Soc.*, 2006, **128**, 4422.
4. H. Fukui, R. Kishi, T. Minami, H. Nagai, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, B. Champagne, E. Botek, and M. Nakano, *J. Phys. Chem. A*, 2008, **112**, 8423.
5. A. S. Katner and R. F. Brown, *J. Heterocycl. Chem.*, 1990, **27**, 563.
6. **1**: yellow prisms; mp 100.0 °C (dec); HRMS (ESI): Calcd for $C_{10}H_8N_2NiS_4$: 370.9700. Found: 370.9730; Anal. Calcd for $C_{10}H_8N_2NiS_4{\bullet}2H_2O$: C, 34.81; H, 4.09; N, 16.24. Found: C, 35.14; H, 3.89; N, 16.31; IR (KBr) cm^{-1}: 3332, 3244, 1509.
7. Crystal data for $Ni(Hapt)_2{\bullet}2H_2O$: $C_{10}H_{10}N_4NiO_2S_2$, $Mw = 341.05$, triclinic, P-1 (#2), $a = 7.1342(13)$, $b = 8.4502(15)$, $c = 12.257(2)$ Å, $\alpha = 76.766(3)$, $\beta = 73.110(3)$, $\gamma = 76.561(4)°$, $V = 677.2(2)$ Å^3, $T = 200$ K, $Z = 2$, ρ(calcd) = 1.672 g cm^{-3}, μ(Mo$K\alpha$) = 1.74 mm^{-1}, reflections collected = 6674, unique reflections = 3069, $R_{\rm int} = 0.083$, param. refined = 193, $R1 = 0.044$ ($I > 2\sigma(I)$), $wR2 = 0.141$ (all data), GOF = 1.05. CCDC-927361.
8. Quantum chemical calculation of **1** was performed at the B3LYP level of theory using Firefly version 7.1.G software package.[9] The double-zeta valence basis set with SBKJC[10] effective-core potential (for Ni atom) as well as the 6-31G basis set (for C, H, N, S atoms) were employed in the calculations.
9. A. A. Granovsky, Firefly version 7.1.G, http://classic.chem.msu.su/gran/firefly/index.html.
10. T. R. Cundari and W. J. Stevens, *J. Chem. Phys.*, 1993, **98**, 5555.