Inorg. Chem. **2003**, *42*, 3534–3539

Inorganic Chemistry
Article

Additional Steps toward Molecular Scale Wires: Further Study of $Ni_5^{10/11+}$ Chains Embraced by Polypyridylamide Ligands

John F. Berry,[†] F. Albert Cotton,*,[†] Peng Lei,[†] Tongbu Lu,[†,‡] and Carlos A. Murillo*,[†]

Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, and School of Chemistry & Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China

Received January 22, 2003

This paper presents two advances in the development of the chemistry of extended metal atom chains (EMACs) that employ di(2-pyridyl)amide (dpa) and its higher homologues (loosely called polypyridylamides). As EMACs employing these ligands are extended to greater lengths, low solubility becomes an increasingly difficult problem. Also, increased stability would be desirable. We have employed a method, which is designed to be applicable to chains of any length, to introduce stabilizing substituents (ethyl groups) on some of the pyridyl rings. We illustrate this here by the synthesis and characterization of the pentanickel complexes $Ni_5(etpda)_4Cl_2 \cdot 6CHCl_3$ and $[Ni_5(etpda)_4](PF_6)_3 \cdot 4Me_2CO$, etpda = the anion of *N*,*N*′-bis(4-ethylpyridyl)-2,6-diaminopyridine. As we had previously predicted, on the basis of the behavior of $Ni_3(dpa)_4Cl_2$ and $[Ni_3(dpa)_4](PF_6)_3$, oxidation causes marked changes in structure and magnetic behavior indicative of a change of electronic structure that would cause an insulator–conductor transformation. We now demonstrate that this is what occurs not only in the previously known Ni_5 compounds but in the new ethyl-substituted ones.

Introduction

The term *molecular wire* (or *nanowire*) has been used to describe many disparate substances, including carbon nanotubes,[1] other nanotubes,[2] polyalkynes,[3] other doped polymers,[4] and still other entities.[5] The broad concept underlying all uses of the term envisions an elongated array of atoms, the thickness and composition of which may vary greatly,[6] which may be assumed to provide a conductive path for electrons (although in many cases, perhaps the majority, there is little or no direct evidence that this is actually true). The most obvious point of having nanowires is to be able to use them as conductors in nanocircuits,[7] but when the possibility of tuning or controlling their resistance is considered, other applications (resistors, rheostats, or switches) come into view.

The specific definition of a molecular wire that guides work in this laboratory begins with a consideration of what a wire is in the macroscopic world in which we live. This is a long, thin piece of metal covered with organic insulation; a typical example is shown in Figure 1a. With miniaturization as a goal we ask: What is the *reductio ad ultimum* for such a wire?[8] This is a chain of single metal atoms with a proportionately thin layer of insulation, as shown in Figure 1b; the order of magnitude of the reduction factor is 10^{-7}.

Besides the obvious question of “how to do it” the mere statement of this goal raises other questions and considerations. One of the most important is how a chain of single metal atoms behaves stereoelectronically. For an infinite, naked chain of metal atoms this problem was first addressed by Peierls,[9] who showed that an evenly spaced chain is inherently prone to become more stable when the metal to metal distances are alternately long and short. This is known as the Peierls distortion; it has been observed many times[10] and has fundamental relations to the Jahn–Teller[11] and

---

* To whom correspondence should be addressed: cotton@tamu.edu (F.A.C.); murillo@tamu.edu (C.A.M.).

[†] Texas A&M University.

[‡] Sun Yat-Sen University.

(1) (a) Odon, T. W.; Huang, J.; Lieber, C. M. *Ann. N.Y. Acad. Sci.* **2002**, *960*, 203. (b) Rueckes, T.; Kim, K.; Joselevich, E.; Tseng, G. Y.; Cheung, C.-L.; Lieber, C. M. *Science* **2000**, *289*, 94. (c) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.

(2) (a) Duan, X.; Lieber, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 188. (b) Ivanovskii, A. L. *Russ. Chem. Rev.* **2002**, *71*, 175.

(3) (a) Heeger, A. J. *Rev. Mod. Phys.* **2001**, *73*, 681. (b) Shirakawa, H. *Rev. Mod. Phys.* **2001**, *73*, 713. (c) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810. (d) Wong, K.-T.; Lehn, J.-M.; Peng, S.-M.; Lee, G.-H. *Chem. Commun.* **2000**, 2259. (e) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477. (f) Kheradmandan, S.; Heinze, K.; Schmalle, H. W.; Berke, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2270.

(4) MacDiarmid, A. G. *Rev. Mod. Phys.* **2001**, *73*, 701.

10.1021/ic034071l CCC: $25.00

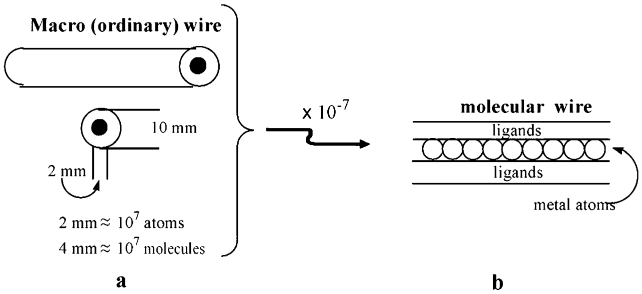


Figure 1. A macrowire (a) and a molecular wire (b) as defined in this work.

Renner[12] effects in discrete molecules. It is also manifested in the fact that the difference between the long (approximately single) bonds and short (approximately double) bonds in polyolefins, $X(CH{=}CH)_nX$, never becomes zero, no matter how great n becomes, but instead reaches a limit of about 0.08 Å (i.e., the difference between about 2.36 and 2.44 Å).[13] Distortions in chains that might be expected to be evenly spaced are also known to arise when there are charge density waves.[14] While, at first sight, these considerations might be thought to bode ill for making molecular wires of the type implied in Figure 1b, this may not be so. For example, there are flaws in the analogy to the Peierls distortion. One is that the molecular wires we propose to make will not be infinite and the boundary conditions will have an effect—although not an easily predicted one—on the M−M interactions; also, because the chains[15] are finite one does not expect to have all M−M distances exactly equal in any case except when there are only three. Another major factor is that the chain of metal atoms will not be naked in the molecular wire and the "insulation" cannot be passive since it will be chemically bonded to the metal atoms and therefore its own chemical properties (including its capacity to conduct electrons) will be intimately coupled to the properties of the metal atom chain itself.

While theoretical guidance is, as always in science, welcome and helpful, experimental exploration of the properties of extended metal atom chains (EMACs) is the most important thing to do, and we continue to pursue this approach vigorously. Very recently we reported that non-metal−metal-bonded $Ni_3(dpa)_4Cl_2$ can be oxidized, giving rise to metal−metal bond formation.[16] This suggests that a switch could be created by manipulation of the electrode potentials. Unfortunately the potential for this particular oxidation process was relatively high and the thermal stability of the oxidized species was low. More recently we showed that the electrode potential for the oxidation of the trinickel molecule can be decreased when an ethyl substituent is incorporated in each of the pyridyl groups. More importantly, the oxidized product appears to be indefinitely stable at room temperature.[17] In our earlier report,[16] we predicted that increasing the length of the chain would also reduce the oxidation potential. In the meantime the laboratory of S.-M. Peng has published a communication on oxidized pentanickel compounds with the ligand tripyridyldiamide (tpda),[18] but they did not study the electrochemistry. We have done this, and here we also present our results using pentanickel chains

---

(5) (a) Venkataraman, L.; Lieber, C. M. *Phys. Rev. Lett.* **1999**, *83*, 5334. (b) Iengo, E.; Zangrando, E.; Minatel, R.; Alessio, E. *J. Am. Chem. Soc.* **2002**, *124*, 1003. (c) Karzazi, Y.; Cornil, J.; Brédas, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 10076. (d) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60. (e) Alvaro, M.; Ferrer, B.; García, H.; Lay, A.; Trinidad, F.; Valenciano, J. *Chem. Phys. Lett.* **2002**, *356*, 577. (f) Le Stang, S.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 1035. (g) Taylor, P. N.; O'Connell, M. J.; McNiell, L. A.; Hall, M. J.; Aplin, R. T.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3456. (h) Jestin, I.; Frère, P.; Blanchard, P.; Roncali, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 942. (i) Shiotsuka, M.; Yamamoto, Y.; Okuno, S.; Kitou, M.; Nozaki, K.; Onaka, S. *Chem. Commun.* **2002**, 590. (j) Jaquinod, L.; Siri, O.; Khoury, R. G.; Smith, K. M. *Chem. Commun.* **1998**, 1261. (k) Schenning, A. P. H. J.; Martin, R. E.; Ito, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Chem. Commun.* **1998**, 1013. (l) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1. (m) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (n) Jiang, B.; Yang, S. W.; Bailey, S. L.; Hermans, L. G.; Niver, R. A.; Bolcar, M. A.; Jones, W. E., Jr. *Coord. Chem. Rev.* **1998**, *171*, 365. (o) Sirota, M.; Minkin, E.; Lifshitz, E.; Hensel, V.; Lahav, M. *J. Phys. Chem. B* **2001**, *105*, 6792. (p) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705. (q) Finniss, G. M.; Canadell, E.; Campana, C., Dunbar, K. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2772. (r) Pruchnik, F. P.; Jakimowicz, P.; Ciunik, Z.; Stanislawek, K.; Oro, L. A.; Tejel, C.; Ciriano, M. A. *Inorg. Chem. Commun.* **2001**, *4*, 19.

(6) The field of extended linear chain compounds and extended structures has been reviewed by a myriad of experts. See for example: (a) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1. (b) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 2. (c) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1983; Vol. 3. (d) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH Publishers: New York, 1988. (e) Bera, J. K.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4453.

(7) (a) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (b) Treboux, G. *J. Phys. Chem. B* **2000**, *104*, 9823. (c) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C.-W.; Chen, J.; Wang, W.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118.

(8) In considering this version of a molecular wire, one might also recall Feynman's often quoted adage that "There is plenty of room at the bottom," by which he meant making devices as small as possible. This version might be called "the bottom of the bottom." See: Feynman, R. P. *Engineering and Science* (CalTech), February 1990.

(9) Peierls, R. E. *Quantum Theory of Solids*; Oxford University Press: Oxford, 1955; p 108.

(10) See for example: (a) Schere-Miller, I.; Böttcher, P. *Z. Kristallogr.* **1991**, *196*, 137. (b) Furuseth, S.; Fjellvåg, H. *Acta Chem. Scand.* **1991**, *45*, 694. (c) Haneveld, A. J. K.; Jellinek, F. *J. Less-Common Met.* **1970**, *21*, 45. (d) Stöwe, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1419. (e) Wu, E. J.; Pell, M. A.; Ibers, J. A. *J. Alloys Compd.* **1997**, *255*, 106. (f) Krönert, W.; Plieth, K. *Z. Anorg. Allg. Chem.* **1965**, *336*, 207. (g) Ben Salem, A.; Meerschaut, A.; Rouxel, J. *C. R. Acad. Sci., Ser. 2* **1984**, *299*, 617. (h) Choi, K.-S.; Patschke, R.; Billinge, S. J. L.; Waner, M. J.; Dantus, M.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1998**, *120*, 10706. (i) Huang, F. Q.; Brazis, P.; Kannewurf, C. R.; Ibers, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 80.

(11) Bersuker, I. B. *The Jahn−Teller Effect and Vibronic Interactions in Modern Chemistry*; Plenum Press: New York, 1984.

(12) Renner, E. *Z. Phys.* **1934**, *92*, 172.

(13) (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London* **1959**, *A251*, 172. (b) Salem, L.; Longuet-Higgins, H C. *Proc. R. Soc. London* **1960**, *A255*, 435. (c) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London* **1960**, *A257*, 445. (d) Yannoni, C. S.; Clarke, T. C. *Phys. Rev. Lett.* **1983**, *51*, 1191. (e) Guo, H.; Paldus, J. *Int. J. Quantum Chem.* **1997**, *63*, 345.

(14) (a) Cody, J. A.; Ibers, J. A. *Inorg. Chem.* **1995**, *34*, 3165. (b) Dung, N.-H.; Pardo, M.-P.; Boy, P. *Acta Crystallogr.* **1983**, *C39*, 668.

(15) Others have referred to the aligned metal atoms as "strings" (Lai, S.-Y.; Lin, T.-W.; Chen, Y.-H.; Wang, C.-C.; Lee, G.-H.; Yang, M.-H.; Leung, M.-K.; Peng, S.-M. *J. Am. Chem. Soc.* **1999**, *121*, 250).

(16) Berry, J. F.; Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *J. Am. Chem. Soc.* **2002**, *124*, 3212.

(17) Berry, J. F.; Cotton, F. A.; Lu, T.; Murillo, C. A.; Wang, X. *Inorg. Chem.*, in press.

(18) Yeh, C. Y.; Chiang, Y.-L.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **2002**, *41*, 4096.

with an ethyl-substituted ligand, etpda, which not only significantly reduces the oxidation potential but also modifies the solubility in common organic solvents. With the unsubstituted polypyridylamide compounds, low solubility is a problem, which gets worse with increasing chain length. The new compounds are $Ni_5(etpda)_4Cl_2$ (**1**) and $Ni_5(etpda)_4(PF_6)_3$ (**2**), and we shall make some comparisons with the previously reported tpda compound $Ni_5(tpda)_4Cl_2$ (**3**) (which we have restudied) and the oxidized $Ni_5(tpda)_4(OTf)_3$ (**4**).

Experimental Section

Materials and Methods. Unless otherwise specified, synthetic procedures were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified by distillation over an appropriate drying agent in a nitrogen atmosphere prior to use. The compounds 4-ethylpyridine, 2,6-dibromopyridine, Bu^tOK, 1,3-bis(diphenylphosphino)propane (dppp) and naphthalene were purchased from Aldrich. Anhydrous $NiCl_2$, $AgPF_6$, and $Pd_2(dba)_3$ (dba = *trans*,*trans*-dibenzylideneacetone) were purchased from Strem Chemicals. 2-Amino-4-ethylpyridine was prepared according to a published method.[19]

Physical Measurements. Unless otherwise specified, solvents of crystallization were removed from samples by placing them under vacuum prior to measurements. IR spectra were taken on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. ^1H NMR spectra were obtained on a Varian XL-300 spectrometer. Elemental analyses were performed by Canadian Microanalytical Services in British Columbia, Canada.

The cyclic voltammograms in CH_2Cl_2 of **1** and **3** (0.5 and 0.1 mM, respectively) were taken on a BAS 100 electrochemical analyzer with $Bu^n{}_4NPF_6$ (0.1 M) electrolyte, Pt working and auxiliary electrodes, a Ag/AgCl reference electrode, and a scan rate of 100 mV/s.

Magnetic susceptibility data for **1**−**3** were collected on a Quantum Design SQUID (superconducting quantum interference device) magnetometer MPMS-XL, with a field of 1000 G as the temperature was increased from 2 to 300 K. A correction was made for the diamagnetic contribution prior to data analysis.

***N*,*N*′-Bis(4-ethylpyridyl)-2,6-diaminopyridine (H_2etpda).** H_2etpda was synthesized following a procedure using a palladium catalyst to aid carbon−nitrogen bond formation.[20] Toluene (500 mL) was added to a mixture of 2-amino-4-ethylpyridine (6.1 g, 50 mmol), 2,6-dibromopyridine (4.7 g, 20 mmol), Bu^tOK (13.4 g, 12.0 mmol), $Pd_2(dba)_3$ (0.84 g, 0.80 mmol), and 1,3-bis(diphenylphosphino)propane (dppp, 0.66 g, 0.16 mmol). This mixture was stirred at 80 °C under a nitrogen atmosphere for 3 days. After cooling to room temperature, 200 mL of water was added. Two phases formed. The organic phase was saved, and the aqueous phase was extracted with chloroform (2 × 100 mL). The organic phases were combined and dried over $MgSO_4$, and then the solvent was evaporated under vacuum to give a red-brown solid. After washing with CH_2Cl_2, the solid was recrystallized from THF giving a pale yellow microcrystalline solid (3.0 g, 51%). ^1H NMR ($CDCl_3$, 300 MHz, δ): 8.93 (s, 2H), 8.16 (d, $J = 5.1$ Hz, 2H), 7.53 (t, $J = 7.8$ Hz, 1H), 7.18 (s, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 6.68 (d, $J = 6.6$ Hz, 2H), 2.62−2.54 (q, $J = 7.5$ Hz, 4H), 1.22 (t, $J = 7.7$ Hz, 6H). Full structural details based on an X-ray crystal structure are in the Supporting Information.

$Ni_5(etpda)_4Cl_2$, 1. A 100 mL round-bottom flask was charged with anhydrous $NiCl_2$ (0.39 g, 3.0 mmol), H_2etpda (0.64 g, 2.0 mmol), and naphthalene (15 g). The mixture was heated to 190−195 °C for 30 min, and then *n*-butanol (5 mL) was carefully added without protection from air; heating was continued while the flask was open to air but with a nitrogen purge until the *n*-butanol was completely evaporated. Then, a solution of Bu^tOK (0.45 g, 4.0 mmol) in 5 mL of *n*-butanol was added dropwise. Heating was continued until the remaining *n*-butanol evaporated completely. The mixture was allowed to cool to about 80 °C, and hexanes were used to wash out naphthalene (4 × 40 mL). After further washing with toluene (3 × 20 mL), the remaining deep purple solid was extracted with chloroform. Then, this solution was layered with hexanes. Deep purple crystals of $Ni_5(etpda)_4Cl_2{\cdot}6CHCl_3$ formed after 2 weeks. The crystals were filtered off, washed with hexanes, and dried under vacuum. Yield: 0.42 g, 51%. Anal. Calcd for $C_{76.2}Cl_{2.6}H_{76.2}N_{20}Ni_5$ ($Ni_5(etpda)_4Cl_2{\cdot}0.2CHCl_3$): C, 55.21; H, 4.60; N, 16.89. Found: C, 55.09; H, 4.73; N, 16.72. IR (KBr, cm^{-1}): 3752 (w), 3448 (br, w), 2965 (m), 2374 (w), 1608 (s), 1572 (m), 1537 (s), 1405 (s), 1404 (vs), 1336 (s), 1263 (m), 1229 (m), 1157 (s), 1097 (m), 1057 (m), 1010 (m), 811 (m), 461 (w).

$Ni_5(etpda)_4(PF_6)_3$, 2. A flask containing $Ni_5(etpda)_4Cl_2$ (0.40 g, 0.25 mmol) and $AgPF_6$ (0.22 g, 0.86 mmol) was charged with 30 mL of $CHCl_3$ at 0 °C. The resulting solution was stirred at 0 °C while protected from light for 0.5 h to give a deep green mixture, which was filtered through Celite to remove AgCl and Ag. The chloroform was evaporated under vacuum, the remaining dark green solid was extracted with 20 mL of acetone, and the extract was filtered. The solution was layered with hexanes and kept in a freezer. After about 1 week, dark green crystals of $Ni_5(etpda)_4(PF_6)_3{\cdot}4C_3H_6O$ formed. The crystals were collected, washed with hexanes, and dried under vacuum. Yield: 0.43 g, 89%. Anal. Calcd for $C_{76}F_{18}H_{76}N_{20}Ni_5P_3$: C, 45.69; H, 3.80; N, 14.01. Found: C, 45.54; H, 3.95; N, 13.73. IR (KBr, cm^{-1}): 3752 (w), 3435 (br, s), 2966 (w), 2373 (w), 1613 (s), 1536 (w), 1411 (vs), 1323 (br, m), 1228 (w), 1160 (s), 1010 (w), 1057 (w), 1019 (w), 842 (s), 557 (m).

X-ray Crystallography. For the X-ray structural studies, each crystal was mounted on a quartz fiber with a small amount of grease and transferred to a goniometer head. Data were collected on a Bruker SMART 1000 CCD area detector system. Cell parameters were obtained using SMART[21] software. Data were corrected for Lorentz and polarization effects using the program SAINTPLUS.[22] Absorption corrections were applied using SADABS.[23] The positions of most of the non-hydrogen atoms were found by the direct methods program in SHELXTL.[24] Subsequent cycles of least-squares refinements followed by difference Fourier syntheses revealed the positions of the rest of the non-hydrogen atoms. Ethyl groups in **1** and some solvent molecules were disordered. All hydrogen atoms were included in idealized positions. Compound **2** was refined as a racemic twin. Important crystallographic data are given in Table 1.

Results

The ligand precursor H_2etpda is the first reported example of a substituted polypyridylamine, and compounds **1** and **2**

---

(19) Hansch, C.; Carpenter, W.; Todd, J. *J. Org. Chem.* **1958**, *23*, 1924.

(20) Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 7240.

(21) *SMART V5.05 Software for the CCD Detector system*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(22) *SAINTPLUS V5.05 Software for the CCD Detector system*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(23) *SADABS*. Program for absorption correction using SMART CCD based on the method of Blessing: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

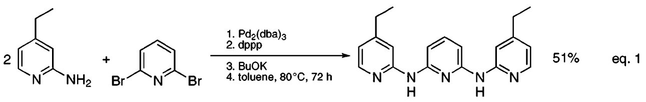
(24) *SHELXTL*, version 6.10; Bruker AXS Inc.: Madison, WI, 2000.

Table 1. X-ray Crystallographic Data for **1** and **2**

	1·6CHCl$_3$	**2**·4C$_3$H$_6$O
empirical formula	$C_{82}H_{82}Cl_{20}N_{20}Ni_5$	$C_{88}H_{100}F_{18}N_{20}Ni_5O_4P_3$
fw	2350.23	2230.34
space group	*C*2/*c*	*I*4
a, Å	16.741(2)	16.3605(4)
b, Å	26.753(3)	16.3605(4)
c, Å	22.584(3)	17.784(1)
α, deg	90	90
β, deg	95.167(2)	90
γ, deg	90	90
Z	4	2
T, K	213	213
λ, Å	0.71073	0.71073
d_{calcd}, g/cm^3	1.550	1.556
μ, mm^{-1}	1.501	1.118
R1^a (wR2^b) ($I > 2\sigma(I)$)	0.0799 (0.1913)	0.0407 (0.1139)
R1^a (wR2^b) (all data)	0.1264 (0.2224)	0.0496 (0.1259)

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

are the first examples of EMACs in which such a ligand has been used. All three compounds were prepared in practical yields as indicated in eqs. 1, 2, and 3, respectively. All three have been structurally characterized by single-crystal X-ray crystallography.



$$5NiCl_2 + 4H_2etpda \xrightarrow[\text{BuOK, 195°C}]{\text{naphthalene}} Ni_5(etpda)_4Cl_2\ (\mathbf{1}) \qquad 51\% \qquad \text{eq. 2}$$

$$Ni_5(etpda)_4Cl_2 + 3AgPF_6 \xrightarrow{CH_2Cl_2} Ni_5(etpda)_4(PF_6)_3\ (\mathbf{2}) \qquad 89\% \qquad \text{eq. 3}$$

The ligand itself shows no unexpected features. The individual molecule is the asymmetric unit, and the crystal contains two relatively long intermolecular N−H···N hydrogen bonds per molecule. The N···N separations are 3.099(2) and 3.114(2) Å.

The structures of **1** and **2** are shown in Figures 2 and 3, respectively. For **2** only the $Ni_5(etpda)_4^{3+}$ ion is shown. The principal bond distances and angles are listed in Table 2. The magnetic data for **1**−**3** are displayed in Figure 4 where the pertinent fitting parameters are also shown.

The electrochemical behavior of **1** is shown in Figure 5 for a CH_2Cl_2 solution with potentials referenced to Ag/AgCl and using Bu_4NPF_6 as the electrolyte. There is a reversible wave at $E_{1/2} = 0.409$ V. Since the electrochemical results for $Ni_5(tpda)_4Cl_2$ (**3**) have not been reported, we prepared $Ni_5(tpda)_4Cl_2$ using the published method[25,26] and confirmed the product by using X-ray crystallography. In CH_2Cl_2 solution and using conditions similar to those for **1**, the oxidation wave is at an $E_{1/2}$ of 0.517 V. This indicates that the ethyl-substituted complex is much more readily oxidizable. The difference in the oxidation potential of over 100 mV is very significant and is reflected in the significant stability of **2**.

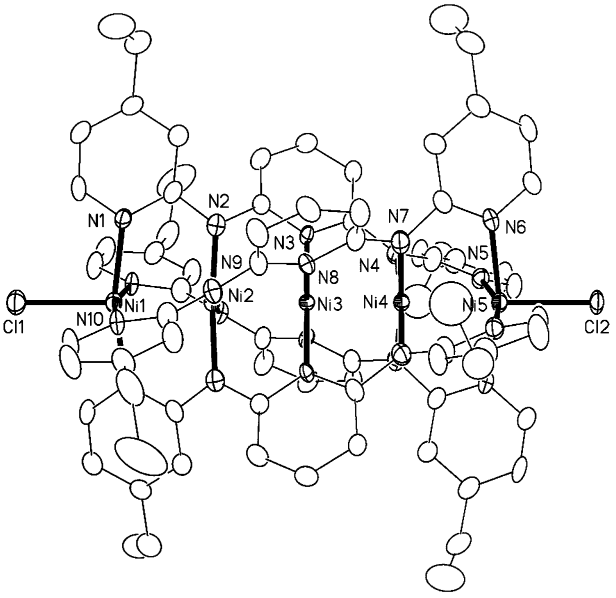


Figure 2. The molecular structure of $Ni_5(etpda)_4Cl_2$, **1**. The thermal ellipsoids are drawn at the 30% probability level, hydrogen atoms have been omitted, and only one orientation of the disordered ethyl groups is shown.

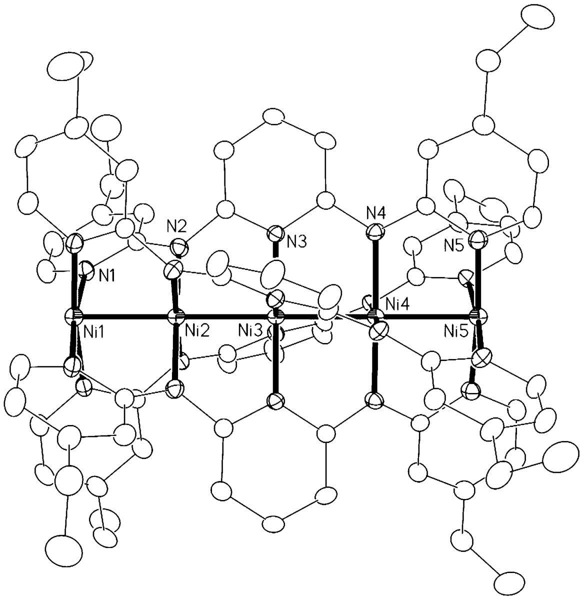


Figure 3. The structure of the cation, $[Ni_5(etpda)_4]^{3+}$, in **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

The two most striking results are that oxidation of the $Ni_5(etpda)_4^{2+}$ entity to $Ni_5(etpda)_4^{3+}$ causes (1) significant changes in Ni−Ni distances and (2) a change from four unpaired electrons to one unpaired electron.

Discussion

In structure and magnetism $Ni_5(etpda)_4Cl_2$ (**1**) resembles the unsubstituted homologue $Ni_5(tpda)_4Cl_2$. In both cases, as shown in Table 3, the inner Ni···Ni distances are shorter than the outer ones by about 0.08 Å. Again, the Ni−N distances for the three inner Ni atoms are similar and much shorter than for the outer ones by about 0.1 Å. These observations are in accord with the view that the three inner

---

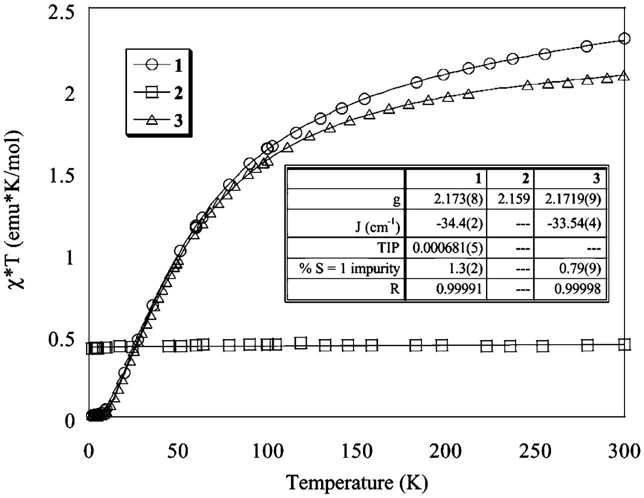
(25) Shieh, S.-J.; Chou, C.-C.; Lee, G.-H.; Wang, C.-C.; Peng, S.-M. *Angew. Chem., Int. Ed. Engl.* **1997** *36*, 56.

(26) Wang, C.-C.; Lo, W.-C.; Chou, C.-C.; Lee, G.-H.; Chen, J.-M.; Peng, S.-M. *Inorg. Chem.* **1998**, *37*, 4059.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

	1		
Ni(1)−Ni(2)	2.389(2)	Ni(2)−Ni(3)	2.304(2)
Ni(3)−Ni(4)	2.304(2)	Ni(4)−Ni(5)	2.383(2)
Ni(1)−Cl(1)	2.375(4)	Ni(5)−Cl(2)	2.369(3)
Ni(1)−N(1)	2.095(7)	Ni(1)−N(10)	2.112(8)
Ni(2)−N(9)	1.914(8)	Ni(2)−N(2)	1.910(8)
Ni(3)−N(8)	1.901(7)	Ni(3)−N(3)	1.907(7)
Ni(4)−N(7)	1.891(8)	Ni(4)−N(4)	1.881(8)
Ni(5)−N(6)	2.113(8)	Ni(5)−N(5)	2.122(8)
N(1)−Ni(1)···Ni(5)−N(5)[a]	86.5	N(10)−Ni(1)···Ni(5)−N(6)[a]	84.2
	2		
Ni(1)−Ni(2)	2.289(2)	Ni(2)−Ni(3)	2.233(2)
Ni(3)−Ni(4)	2.235(2)	Ni(4)−Ni(5)	2.292(2)
Ni(1)−N(1)	1.931(4)	Ni(2)−N(2)	1.876(3)
Ni(3)−N(3)	1.912(3)	Ni(4)−N(4)	1.909(3)
Ni(5)−N(5)	1.907(4)		
N(1)−Ni(1)···Ni(5)−N(5)[a]	83.8		

[a] These values refer to the overall torsion angle of the compound (i.e., the sum of the torsion angles along each Ni···Ni vector).



	1	2	3
g	2.173(8)	2.159	2.1719(9)
J (cm^{-1})	-34.4(2)	---	-33.54(4)
TIP	0.000681(5)	---	---
% S = 1 impurity	1.3(2)	---	0.79(9)
R	0.99991	---	0.99998

Figure 4. The magnetic behavior of compounds **1**−**3**. Solid lines are least-squares fits, and important parameters are given in the inset. The antiferromagnetic coupling for **1** and **3** is evident, whereas the Curie law behavior for **2** is clear.

nickel atoms are essentially low-spin in square coordination, while the outer ones are high-spin in square pyramidal coordination and that there are no Ni−Ni bonds.

The shortening in Ni−Ni distances from **1** to **2** is significant, especially as it might have been expected that an increase in the positive charge would increase repulsion between the positively charged Ni atoms which would lead to an increase in metal−metal distances. For the two inner Ni−Ni distances, the decrease is 0.07 Å, and for the outer ones, it is 0.09−0.10 Å. We believe that the shortening in Ni−Ni separations can be accounted for by formation of metal−metal bonds.[27] Such behavior parallels that of $Ni_3(dpa)_4Cl_2$, for which the Ni···Ni separation decreases by 0.15 Å from 2.43 to 2.28 Å upon oxidation to $Ni_3(dpa)_4(PF_6)_3$. A similiar effect is observed in the oxidation of $Ni_3(depa)_4Cl_2$ to $Ni_3(depa)_4(PF_6)_3$.[17] Contrarily, for the corresponding Cu analogue, $Cu_3(dpa)_4Cl_2$, oxidation to $[Cu_3(dpa)_4Cl_2]SbCl_6$ causes an increase of 0.04 Å in Cu···Cu separations, from 2.47 to 2.51 Å.[28] In the latter there is no Cu−Cu bond and therefore the increase in Cu···Cu separation is due to the increase in the electrostatic charge upon oxidation.

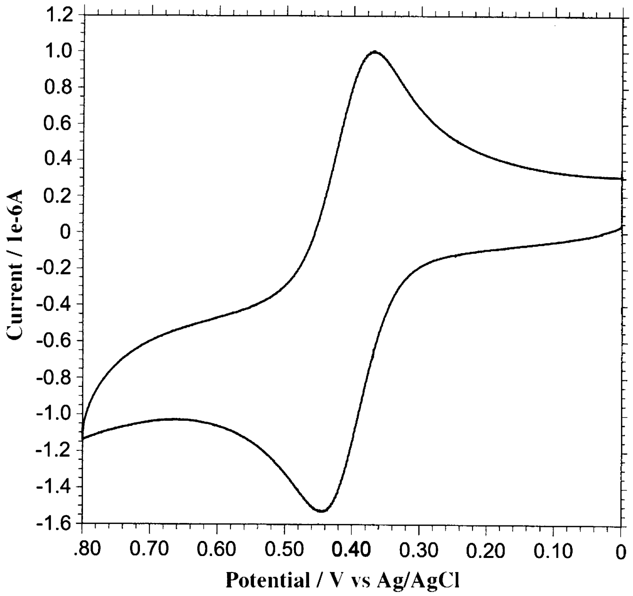


Figure 5. The cyclic voltammogram of $Ni_5(etpda)_4Cl_2$ (**1**) in CH_2Cl_2.

Magnetic Susceptibility Results. Measurements have been made for both $Ni_5(etpda)_4Cl_2$ (**1**) and the oxidized compound, $Ni_5(etpda)_4(PF_6)_3$ (**2**), in samples from which solvent of crystallization had been removed to eliminate the possible uncertainty as to the composition of the crystals since solvent is easily lost. The results are shown in Figure 4. It is clear that, for the latter, the χT value is temperature-independent within experimental error and corresponds to one unpaired electron with a g value of 2.159. For $Ni_5(etpda)_4Cl_2$, the measured data can be well fitted (correlation coefficient of 0.99991) by the following equation, where $x = J_{15}/kT$ and J is defined by the term $-J_{15}S_1{\cdot}S_5$.[29]

$$\chi = \frac{2Ng^2\beta^2}{kT}\,\frac{(e^x + 5e^{3x})}{(1 + 3e^x + 5e^{3x})}$$

Important values are shown in the inset to Figure 4. We have compared these results with those reported for $Ni_5(tpda)_4(SO_3CF_3)_3$ (**4**) and $Ni_5(tpda)_4Cl_2$ (**3**). There are major differences, especially for the unoxidized compounds. For **4** the reported results indicate that there is one unpaired electron, but quantitatively disagree with those we have obtained for **2**. Peng et al.[18] fitted the data for **4** to a model which assumes that only one of the terminal nickel ions is oxidized to Ni^{3+},

---

(27) In a Ni_5 unit, there are 20 metal-based molecular orbitals which arise from bonding, nonbonding, and antibonding combinations. The 39 electrons of the Ni_5^{11+} unit fill all but the highest antibonding orbital, which is half-filled.

(28) Berry, J. F.; Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2003**, *42*, 2418.

(29) This equation is based on the model given in ref 26 for similar pentanickel systems, in which $S_1 = S_5 = 1$ and $S_2 = S_3 = S_4 = 0$. Antiferromagnetic coupling between S_1 and S_5 is accounted for by the zero-field Hamiltonian $\mathscr{H} = -JS_1{\cdot}S_5$. Use of the eigenvalues from this Hamiltonian and the Van Vleck equation produces the equation given in the text. Though the exchange coupling mechanism is unknown, it is likely to be via spin polarization through the bridging ligands.

Table 3. Some Key Structural Results for **1**, **2**, and Related Compounds of the Type $Ni_5(tripyridyldiamide)_4X_2^{n+}$, $n = 0, 1$

compound	n	range of Ni−Ni distances, Å		range of Ni−N distances, Å		Ni−X, Å	ref
		inner	outer	inner	outer		
1[a]	0	2.304(2)−2.304(2)	2.383(2)−2.389(2)	1.881(8)−1.914(8)	2.097(7)−2.122(8)	2.369(3)−2.375(4)	*c*
2[a]	1	2.233(2)−2.235(2)	2.289(2)−2.292(2)	1.876(3)−1.912(3)	1.907(4)−1.931(4)	2.540(8)−2.956(9)	*c*
MCl_2[b] (**3**)	0	2.306(2)−2.306(2)	2.385(2)−2.385(2)	1.88(2)−1.95(2)	2.099(9)−2.113(9)	2.346(3)	26
$M(CN)_2$	0	2.296(2)−2.296(2)	2.400(3)−2.400(3)	1.90(1)−1.92(1)	2.094(7)−2.094(7)	1.95(2)	26
$M(N_3)_2$	0	2.298(2)−2.298(2)	2.379(2)−2.379(2)	1.83(2)−1.96(2)	2.007(8)−2.096(8)	2.007(4)	26
$M(SCN)_2$	0	2.298(2)−2.294(2)	2.367(2)−2.371(2)	1.884(9)−1.907(8)	2.063(9)−2.115(9)	1.998(9)−1.999(9)	26
$[M(CH_3CN)_2](PF_6)_2$	0	2.291(2)−2.291(2)	2.346(3)−2.346(3)	1.71(2)−1.93(1)	2.084(9)−2.123(8)	2.01(1)	26
$[M(H_2O)(BF_4)](BF_4)_2$	1	2.245(1)−2.261(1)	2.300(1)−2.337(1)	1.896(5)−1.911(5)	1.929(5)−2.022(6)	2.252(7)−2.475(4)	18
$[M(SO_3CF_3)_2]SO_3CF_3$ (**4**)	1	2.245(2)−2.276(2)	2.304(2)−2.358(2)	1.874(10)−1.904(9)	1.948(9)−2.08(1)	2.059(7)−2.338(8)	18

[a] For **1** and **2**, the ligand is the ethyl-substituted etpda. For all others it is the nonsubstituted tpda. [b] M stands for the $Ni_5(tpda)_4$ unit. [c] This work.

and that antiferromagnetic coupling between the spins at either end of the molecule is responsible for the observed μ_{eff} of ~2.0 μ_B at low temperatures. This leads to J values of −8.3 and −555 cm^{-1} for **3** and **4**, respectively. The difference of over 500 cm^{-1} is unrealistic, and therefore such a model is highly suspect. There is a large temperature-independent paramagnetism (TIP) in the data for **4** (typically due to impurities in the sample) which causes the μ_{eff} to rise at higher temperatures. This commonly leads to misinterpretation of the magnetic data.[30] It appears that, once corrected for this TIP, the data for **4** should follow the Curie law for $S = {}^1/_2$.

Even more marked is the discrepancy between the results for the unoxidized compounds. According to ref 26, magnetic susceptibility data for four $Ni_5(tpda)_4X_2$ compounds, with $X = Cl^-$, CN^-, N_3^-, and NCS^-, all lead to J values[31] in the range of −12.80 to −18.48 cm^{-1}. These are all 0.25−0.39 of the value we have obtained by carefully remeasuring $Ni_5(tpda)_4Cl_2$, **3** (Figure 4). Moreover, we have obtained an excellent fit to the χT vs T data without the use of a Weiss constant. Indeed, there is nothing in our data for **3**, nor in the data in ref 26, to suggest that the inclusion of a Weiss constant is even appropriate, let alone necessary. Nevertheless, Peng et al.[26] included an extremely large one (−44.47 K) in fitting their data, without stating any reason for doing so. Probably it is as a consequence of doing this that they obtained very low values of J.

Thus, after careful examination of the magnetic data for **1** and **2**, and re-examination of **3** and **4**, the important conclusion to be drawn is that the pentanickel complexes of etpda and tpda behave similarly. Unoxidized compounds have no Ni−Ni bonds, but high-spin terminal Ni atoms; oxidized species have a delocalized electronic structure, one unpaired electron, and partial Ni−Ni bonds. However, the ethyl-substituted compounds are significantly more stable in the oxidized form. This additional stability represents a significant step toward making molecule scale devices from polypyridyl complexes an achievable reality.[32]

Acknowledgment. This work was supported by the Robert A. Welch Foundation and through a Nanoscale Science and Engineering/NIRT Grant (DMR-0103455) and the Telecommunications and Information Task Force at Texas A&M University. J.F.B. thanks the National Science Foundation for support in the form of a predoctoral fellowship.

Supporting Information Available: Crystallographic data in CIF format for **1**, **2**, and H_2etpda and an ORTEP plot of the latter as a PDF file. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034071L

---

(30) Escuer, A.; Ribas, J. *J. Chem. Soc., Dalton Trans.* **2002**, 3778.

(31) In ref 26 J_{15} is defined so that it should be one-half of our J_{15}. The numbers given here, for comparison, are therefore twice the values listed in ref 26. We also note that in ref 26 there are errors in eqs 5 and 6, but it is impossible to tell whether these are only typographical errors, or whether the incorrect equations were actually used.

(32) It should be noted that even though oxidation of **1** to **2** changes the electronic structure as to favor application to devices such as reversible molecular switches, such oxidation is accompanied by significant chemical changes (i.e., removal of axial chloride ions). Currently we are studying ways to eliminate exchange of axial ligands.