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Influence of Electron-Attractor Substituents on the Magnetic Properties of Ni(II) String Complexes

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Density functional theory calculations carried out on the anionic Ni(II) chain complexes {trinickeltetrakis[2,6-bis(amido)pyridine]}$^{2-}$ and {trinickeltetrakis[*N*,*N′*-bis(sulfonyl)pyridyldiamido]}$^{2-}$ show that the electron-attractor character of the sulfonyl substituent modifies the basicity of the amido ligand ends so as to raise the electronic state of the underlying metal atom from low spin ($S = 0$) to high spin ($S = 1$). The computed elongation of the outermost Ni–N bonds with the grafting of SO_2H substituents is in agreement with this interpretation.

Extended metal atom chains held together by means of four poly(pyridylamide) (ppa) ligands represent an extended family of complexes exhibiting versatile structural, magnetic, and conducting properties, sometimes unprecedented.[1−3] Even though such complexes have been characterized with a large variety of transition metals,[1] nickel—and, to a lesser extent, chromium—has been widely used in recent reports to explore the potentialities of this new chemistry. Recent advances in the synthesis and characterization of Ni(II) strings have extended the size of the linear metal framework up to nine atoms.[4] The possibility of attaching ligands in the axial position at both ends of the metal framework has been used to assemble complex molecular architectures[5] and to explore and tune the properties of the metal strings.[6] The standard ppa anions of the general formula $[C_5H_4N(NC_5H_3N)_n\text{-}NC_5H_4N]^{(n+1)-}$, which can attach an odd number of metal atoms, have been modified so as to become *even-dentate* ligands and give rise to linear-chain complexes with four or six metal atoms.[1,7] Examples of such modified ppa ligands are (i) the *N*-phenyldipyridyldiamido (phdpda) dianion and (ii) the *N*-(*p*-toluenesulfonyl)dipyridyldiamido (tsdpda) dianion, which were used for the synthesis of the $Ni_4(\mu_4\text{-phdpda})_4$ (**1**) and $Ni_4(\mu_4\text{-Tsdpda})_4(H_2O)_2$ (**2**) complexes, respectively,[8,9] whose recent theoretical analysis[9] is at the origin of the present work. In the same spirit, the tridentate 2,6-bis(phenylamido)pyridine ($BPAP^{2-}$) dianion was schematically deduced from the standard dipyridylamide (dpa) monoanion by just inverting the amido and the pyridyl positions in the ligand structure (Chart 1). The $[Ni_3(BPAP)_4]^{2-}$ complex (**3**), together with its chromium homologue, has been characterized by Cotton et al.[10]

All Ni(II) metal strings stabilized with standard ppa ligands and completed in the axial position with two L^- ligands were shown to exhibit antiferromagnetic coupling between the outermost metal atoms,[4,6] whose electronic state was raised to high spin ($S = 1$) as a consequence of the square-pyramidal field induced by the axial ligand and the four pyridyl ends. At variance with that, complexes **1** and **3** are both devoid of axial ligands *and* their ground state is

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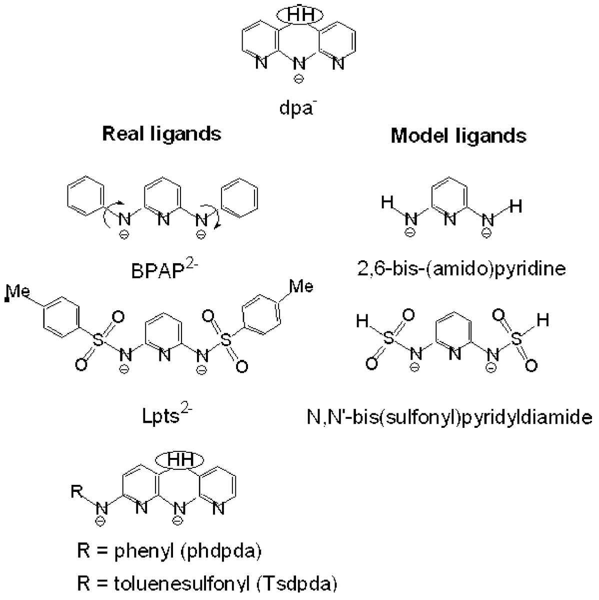
Chart 1



diamagnetic. The link between the structure and the magnetic behavior was clearly made by Cotton et al., telling that "unless there are axial ligands present, chains of Ni(II) atoms simply consist of stacked square, diamagnetic NiN_4 units".[10] The change of the magnetic state induced by the loss of axial coordination was later corroborated by density functional theory (DFT) calculations carried out first on the hypothetical complex $[Ni_3(dpa)_4]^{2+}$ [11] and then on a model of **1**.[9] It was interpreted in terms of the creation of a large highest occupied molecular orbital−lowest unoccupied molecular orbital gap mainly due to the stabilization of the σ-type molecular orbitals (MOs) of the metal framework resulting from the loss of the antibonding interaction with the axial ligands (Figure 1).

Calculations carried out on a model of complex **2**[9] and on its hypothetical derivative deprived of axial water ligands raised a problem, however. The dihydrated complex was rightly predicted to be antiferromagnetic, but the removal of the water molecules, carried out at the DFT level, did not modify the antiferromagnetic nature of the ground state. Because the only major difference between the hypothetical $Ni_4(\mu_4\text{-Tsdpda})_4$ (**4**) and the diamagnetic complex **1** resides in the presence of four electron-attractor tosylate substituents on the terminal amido groups of **4**, we concluded that a tuning of the basicity at the ends of the polydentate equatorial ligand could also influence the magnetic state of the complex.[9] To check this conjecture, we report DFT calculations[12] carried with *Gaussian03*[13] on two trinuclear chain complexes of Ni(II): (i) a model of **3** in which the phenyl substituents of the BPAP ligands have been removed and replaced with hydrogens (**3′**) and (ii) a hypothetical dianion also derived from $[Ni_3(BPAP)_4]^{2-}$ by replacing the phenyls of BPAP by electron-attractor SO_2H substituents (**5**; Figure 2). While this study was in progress, we became aware of an experimental work by Peng et al. reporting the synthesis of the *N*,*N′*-bis(*p*-toluenesulfonyl)pyridyldiamido ($Lpts^{2-}$) ligand modeled in **5** and its use in the synthesis of a series of neutral trinuclear chain complexes of Ni(II) combining in the same molecule Lpts and the standard dpa ligands.[14]

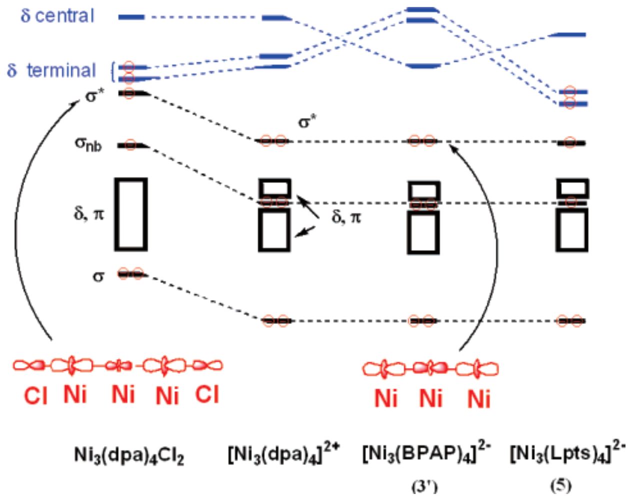


Figure 1. Qualitative orbital energy diagram adapted from DFT calculations on a series of trinickel complexes. Removing the axial ligands stabilizes all σ-type MOs and generates an energy gap, with the δ-type MO set exhibiting Ni−N antibonding character (displayed in blue). Then, inverting the pyridyl and amido ends modifies the energy sequence of the δ MOs. Eventually, grafting electron-attractor substituents sufficiently lowers the energy of the δ MOs localized on terminal atoms to restore the quintet state as the single determinant state of lowest energy.

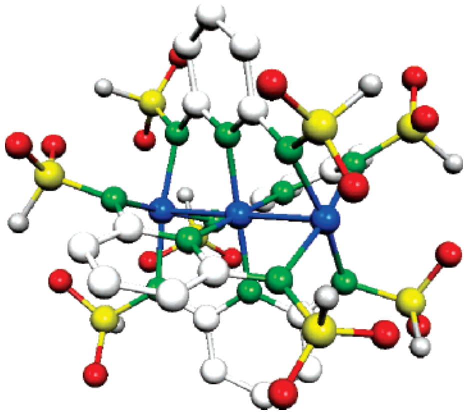


Figure 2. MOLEKEL representation of **5** in the geometry computed for the high-spin (quintet) state. Color code: blue, Ni; green, N; yellow, S; red, O; white, C. H atoms from the pyridine rings are omitted for clarity.

The relative energies obtained for the lowest diamagnetic singlet, triplet, and quintet states of **3′** and **5** in their optimal geometries are displayed in Table 1, together with selected geometrical parameters and atomic spin densities for the

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(12) Calculations and geometry optimizations have been carried out using the DFT formalism with the B3LYP exchange-correlation functional. All-electron valence double-ζ basis sets (D95V) were used to describe C, O, and H atoms. Full double-ζ (D95) bases were used, supplemented with one and two d-type polarization functions for N and S, respectively. The valence shell of Ni was described at the double-ζ level, and the Ne core was modeled with the Los Alamos core potential. The antiferromagnetic low-spin state of **3′** has been characterized using the broken-symmetry approach within the framework of the Heisenberg Hamiltonian, defined as $\hat{H} = -2J_{AB}\hat{S}_A\cdot\hat{S}_B$. We used the approximate projection proposed by Yamaguchi et al.[16] More details can be found in ref 9.

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Table 1. Properties Computed for the Lowest States of **3′** and **5**: Relative Energies ($kcal \cdot mol^{-1}$) and Geometrical Parameters (Distances in Angstroms and Angles in Degrees)

	{trinickeltetrakis[2,6-bis(amido)pyridine]}$^{2-}$ (**3′**)				{trinickeltetrakis[*N*,*N′*-bis(sulfonyl)pyridyldiamido]}$^{2-}$ (**5**)			
	singlet (diamagnetic)	triplet	quintet	obsd[a]	singlet (diamagnetic)	triplet	quintet	singlet (antiferromagnetic)
energy	**0.0**	+4.8	+42.7		+1.0	+32.8	**0.0**	**−1.1**[b]
Ni−Ni	2.426	2.381	2.405	*2.368*	2.393	2.392	2.444	2.430
Ni_{inner}−N	1.951	2.045	1.980	*1.906*	1.935	2.013	1.964	1.964
Ni_{outer}−N	1.928	1.939	2.049	*1.918*	1.979	1.999	2.086	2.085
N−Ni−Ni−N[c]	11.0	2.9	18.0	*17.6*	24.2	22.0	26.2	26.4

[a] From ref 10. [b] Broken-symmetry value. [c] Torsion angle computed between the pyridyl and amido N atoms.

open-shell states. For **3′**, the computed ground state is a diamagnetic singlet, in agreement with the ^{1}H NMR data obtained for **3**.[10] The quintet state associated with a high-spin configuration of the terminal Ni atoms subject to antiferromagnetic coupling, which yields the ground state in the series of ppa chain complexes of Ni(II), is in the present case rejected to high energies (Table 1). More unexpectedly, a triplet state, corresponding to a high-spin configuration of the *central* Ni, arises at a relatively low energy (+4.8 $kcal \cdot mol^{-1}$). This results from an energy crossing between the Ni−N antibonding δ MOs localized on the central and terminal atoms (Figure 1) and corroborates the hypothesis according to which the relative strength of the *equatorial* field, stronger with deprotonated amido groups than with pyridyl ends, could contribute in these Ni chains to orient the metal spin state. The geometry computed for the diamagnetic ground state of **3′** is in good agreement with the observed structure of **3**, even though all distances are slightly overestimated (Table 1). Note that the helical torsion of the ligand observed in $[Ni_3(BPAP)_4]^{2-}$ is reproduced by the calculations on **3′**, even though the free bis(amido)pyridine ligand is not constrained as dpa to nonplanarity. Furthermore, the torsion angle appears to be highly dependent on the molecular spin state and, therefore, on the relative lengths of the Ni−N bonds (Table 1). Nonplanarity, therefore, appears as a response of the BPAP-like structure to the variety of Ni−N distances, that is, short around low-spin metal atoms and long around high-spin ones (Table 1).

The grafting of an electron-attractor sulfonyl group to both amido ends of the bis(amido)pyridine model ligand yields a dramatic change in the calculated energy sequence of the three spin states. The quintet state associated with a high-spin configuration for both terminal Ni atoms has been restored as the pure spin state of lowest energy, as for $Ni_3(dpa)_4L_2$ complexes, but without the assistance of axial ligands. As expected, the coupling between the two high-spin terminal Ni atoms gives rise to an antiferromagnetic singlet state lower in energy than the quintet. Using Noodleman's broken-symmetry method[12,15] completed with Yamaguchi's spin projection[12,16] within the Heisenberg Hamiltonian framework, we find for the antiferromagnetic ground state an energy estimate of 1.1 $kcal \cdot mol^{-1}$ below the quintet, corresponding to a magnetic coupling coefficient $-2J$ of 193 cm^{-1}. The energy of the diamagnetic singlet is computed to be very close, however, at +1.0 $kcal \cdot mol^{-1}$ above the quintet and +2.1 $kcal \cdot mol^{-1}$ above the broken-symmetry state. Because of this small energy gap, the prediction of an antiferromagnetic ground state for **5** cannot be asserted with complete confidence, but the trend induced by the electron-attractor substituents is clearly established. Finally, the triplet state associated with a high-spin configuration of the central Ni is now quite destabilized, at +32.8 $kcal \cdot mol^{-1}$ above the quintet. A comparison between the Ni−N distances optimized for the *diamagnetic singlet* states of **3′** and **5** shows that the grafting of sulfonyl substituents to the amide ends *reverses* the relative bond lengths between Ni_{inner}−N and Ni_{outer}−N. The latter is shortest in **3′** because of the more basic character of the deprotonated amido ends, but the presence of electron-attractor substituents mitigates this basicity and results in an elongation of the Ni_{outer}−N bond by 0.05 Å (Table 1). A similar expansion of the Ni_{outer}−N bonds is computed for the paramagnetic states of **5**, compared to the equivalent open-shell states of **3′**. As a consequence of these changes in the constraints imposed to the tridentate ligands, the helical torsion of the coordinated bis(sulfonyl)pyridinediamide is computed to be significantly more important than that for the nonsubstituted ligand.

In conclusion, we show by means of DFT calculations carried out on the $Ni_3^{(6+)}$ chain complexes stabilized by various types of tridentate pyridylamide ligands that the relative basicities of the equatorial ligand ends might be sufficient to influence the ground state and the magnetic properties of the metal framework, even without any contribution from axial coordination.

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Supporting Information Available: Complete reference to the Gaussian software, total energies, symmetry constraints, optimized Cartesian coordinates, Mulliken charges, and atomic spin populations obtained from DFT/UB3LYP calculations carried out on the various spin states of **3′** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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