orientations can have an effect on the spin state of iron(III) porphyrinates. All known[9,22] pyridine-complexed low-spin iron(III) porphyrinates have ϕ angles[23] between 40 and 45°. The few remaining derivatives are not low spin and have ϕ values between 0 and 10°.[6,10] The origin of this orientation effect is in the steric interactions between the pyridine hydrogen atoms and atoms of the core at ϕ values significantly less than 40°: a low-spin axial bond distance (2.03 Å) leads to unreasonably short nonbonded distances. With the foregoing background, we were not surprised to find that the ϕ value for molecule 1, the spin-equilibrium site, is 44°. Molecule 2, the high-spin site, has $\phi \approx 30°$. A second feature that probably weakens the axial ligand field in molecule 2, and hence favors a high-spin state, is the deviation from ideal coordination modes of both axial ligands. The FeNCS group is bent with an apparent Fe–N–C angle of 139°. Further, the plane of the pyridine ring is tilted with a dihedral angle between the pyridine plane and the porphinato plane of 73°. We have previously noted[6] that packing interactions appear responsible for a number of nonlinear MNCS groups that are described in the literature. The geometry of the two axial ligands is normal in molecule 1; the Fe–N–C angle is 175° and the dihedral angle between the pyridine plane and the porphinato plane is 90°.

Interestingly, some aspects of the nonideal coordination geometry of molecule 2 are found in the structure of (NCS)metHb.[3] The Fe–NCS linkage in (NCS)metHb is bent in both subunits. An angle of approximately 120° is observed and is the apparent result of the steric constraints of the heme pocket. It is curious, albeit surely coincidental, that the two molecules in the asymmetric unit of [Fe(TPP)(NCS)(py)] are different magneticially, as is found in the two crystallographically unique hemes in (NCS)-metHb. Although both hemes have a bent thiocyanate, the crystallographic results suggest that the β-heme is high spin and that the α-heme is an equilibrium mixture of high- and low-spin states.[3] However in [Fe(TPP)(NCS)(py)], molecule 1 with the linear Fe–NCS group is involved in the spin equilibrium. The molecule (2) with the bent Fe–NCS is high spin. Further, [Fe(TPP)(NCS)py)]·$^1/_2$py is low spin and has a bent Fe–NCS group.[6] [Fe(OEP)(NCS)(py)] is a high spin and has a linear Fe–NCS group. This lack of correlation between the spin state of the iron(III) center and the Fe–N–C angle suggests that the angle adopted is a result of packing constraints and not π interactions.[24]

Both molecules have essentially planar porphyrin cores. The dihedral angles formed by the peripheral phenyl rings and the porphiato core are 89 and 72° for molecule 1 and 55 and 80° for molecule 2. All are within the normal range.

Summary

The two crystallographically unique molecules in the asymmetric unit of the triclinic phase of [Fe(TPP)(NCS)(py)] exhibit different magnetic behavior. Although the axial ligands are the same, one molecule is high spin and the other is an equilibrium mixture of high- and low-spin states. The two-site interpretation of the magnetic data is independent of the choice of space group. This [Fe(TPP)(NCS)(py)] system further exemplifies the importance of heme environment in determining spin state in (porphinato)iron(III) complexes.

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Registry No. [Fe(TPP)(NCS)(py)], 81602-84-8; Fe(TPP)(NCS), 81877-32-9.

Supplementary Material Available: For [Fe(TPP)(NCS)(py)] at 293 K, Figures 1S and 2S, ORTEP plots of the molecular structure, Table A, final anisotropic temperature factors, Table B, fixed hydrogen atom positions, Table C, rigid-group parameters and derived crystallographic coordinates for the axial ligands, and a table of observed and calculated structure amplitudes (×10) and for [Fe(TPP)(NCS)(py)] at 96 K, Table D, final anisotropic thermal parameters, Table E, fixed hydrogen positions, Table F, rigid-group parameters and derived crystallographic coordinates for the axial ligands, and a table of observed and calculated structure amplitudes (×10) (56 pages). Ordering information is given on any current masthead page.

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π-Donor Character of the Dimethylamido Ligand

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The core electron binding energies of dimethylamides of early transition metals, when qualitatively interpreted in terms of atomic charges, are consistent with nitrogen–metal $p\pi \rightarrow d\pi$ bonding. Further support for such π bonding is obtained by the "localized orbital ionization potential" method, in which one compares the nitrogen lone-pair ionization potentials with the ionization potentials that the nitrogen 2p orbitals would have if they were strictly nonbonding.

Structural data for transition-metal amides show that the nitrogen atom of a terminal amido ligand generally has a planar or almost planar three-coordinate environment. In addition, the M–N distance is usually shorter than the predicted single-bond distance. These observations are usually interpreted as evidence for significant $p\pi \rightarrow d\pi$ bonding between the nitrogen and transition-metal atoms.[1] However, the data are not unequivocal because the length of an M–N single bond is not known experimentally. In addition, the structural features might be due to ionic bonding, with a tight, head-on orientation of the NR$_2^-$ dipole.

In this study we have determined the core electron binding energies of the metal, nitrogen, and carbon atoms in seven homoleptic dimethylamido complexes of the early transition metals. These data can be used to ascertain the importance of N–M $p\pi \rightarrow d\pi$ bonding in two ways. First, the data can be used qualitatively to estimate the relative magnitudes of atomic charges, and these atomic charge data can be interpreted in terms of possible $p\pi \rightarrow d\pi$ bonding. Second, the localized orbital ionization potential (LOIP) method can be used.[2,3] That is, the core binding energies can be used to estimate what the nitrogen lone-pair ionization potentials would be if the lone pairs were strictly

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Table I. Core Binding Energies (eV) of Transition-Metal Dimethylamido Complexes

compd	metal core level[a] E_B	metal core level[a] fwhm[b]	N 1s E_B	N 1s fwhm	C 1s E_B	C 1s fwhm
$Ti[N(CH_3)_2]_4$	461.43 (2)[c]	1.04 (5)	402.93 (2)	1.16 (9)	290.79 (2)	1.36 (4)
$Zr[N(CH_3)_2]_4$	186.27 (2)	1.06 (9)	403.21 (4)	1.06 (14)	291.11 (3)	1.26 (8)
$Hf[N(CH_3)_2]_4$	21.12 (3)	1.24 (9)	403.19 (2)	1.09 (7)	291.02 (2)	1.32 (7)
$Nb[N(CH_3)_2]_5$	210.74 (2)	1.01 (8)	403.03 (3)	1.14 (9)	290.85 (4)	1.33 (12)
$Ta[N(CH_3)_2]_5$	29.84 (5)	1.31 (14)	403.12 (5)	1.61 (16)	290.92 (4)	1.65 (10)
$Mo[N(CH_3)_2]_4$[d]	234.04 (3)	1.11 (12)	403.14 (4)	1.08 (14)	290.66 (3)	1.16 (12)
$W[N(CH_3)_2]_6$	38.46 (2)	1.10 (9)	402.70 (3)	1.01 (12)	290.44 (4)	1.14 (14)

[a] Ti $2p_{3/2}$, Zr $3d_{5/2}$, Hf $4f_{7/2}$, Nb $3d_{5/2}$, Ta $4f_{7/2}$, Mo $3d_{5/2}$, W $4f_{7/2}$. [b] Full width at half-maximum. [c] 2σ value of least-squares fit of spectra indicated parenthetically. [d] Data from: Beach, D. B.; Jolly, W. L., to be submitted for publication.

nonbonding. These values can then be compared with the actual lone-pair ionization potentials to determine the net stabilization or destabilization of the orbitals through interaction with other orbitals of the same symmetry.

Qualitative Atomic Charge Interpretation

The core binding energies are given in Table I. The nitrogen 1s binding energies are all in the neighborhood of 403.0 eV, a reasonable value, considering that the nitrogen binding energy of trimethylamine is 404.8 eV[4] and that in the amides the nitrogen atom is bonded to an atom that is much more electropositive than a methyl group. However, in order to assess the net electron-withdrawing character of the $N(CH_3)_2$ group, it is more instructive to compare the titanium $2p_{3/2}$ binding energy of $Ti[N(CH_3)_2]_4$ (461.43 eV) with the titanium binding energies of $TiCl_4$ (465.4 eV), $TiBr_4$ (464.4 eV), and TiI_4 (463.8 eV).[4] The titanium atom in the amide appears to have a much lower positive charge than the titanium atom of TiI_4. This result would not have been predicted from simple electronegativity considerations and suggests that the nitrogen atoms of the titanium amide donate electron density to the titanium atom by $p\pi \rightarrow d\pi$ bonding. Further indirect evidence for $p\pi \rightarrow d\pi$ bonding can be seen in the fact that the metal binding energies of the molybdenum and tungsten amides are similar to the corresponding values of the hexacarbonyls.[4] (Compare 234.04 eV for $Mo[N(CH_3)_2]_4$ with 234.6 eV for $Mo(CO)_6$. Similarly, compare 38.46 eV for $W[N(CH_3)_2]_6$ with 37.8 eV for $W(CO)_6$ and 46.8 eV for WF_6.)

The LOIP Method

If the nitrogen $p\pi$ lone-pair orbitals of a metal amide did not interact with other orbitals of the molecule, and interacted only weakly among themselves, their net effect would be that of a set of strictly nonbonding molecular orbitals. In that case the "center of gravity" (COG) of their ionization potentials[3,5,6] would approximately equal the localized orbital ionization potential (LOIP) calculated from the lone-pair ionization potential of planar NH_3[7] and the N 1s binding energies of planar NH_3[7] and the metal amide. The LOIP is the value that the $p\pi$ lone-pair ionization potential *would have* if the lone pairs were absolutely noninteractive. In Table II are given the degeneracy-weighted averages (centers of gravity) of the nitrogen lone-pair ionization potentials, taken from the literature,[8,9] together with the corresponding LOIPs.[10] It is instructive to consider the tabulated values of the differences, COG – LOIP. A COG – LOIP value of zero corresponds to no *net* stabilization or destabilization energy for the lone pairs. A negative value implies that interactions of the lone pairs with filled, lower lying orbitals outweigh interactions with empty, higher lying orbitals. A positive value has the opposite implication. In these compounds, the filled, lower lying orbitals that are most likely to interact with the lone pairs are the CH_3 bonding orbitals of the $N(CH_3)_2$ groups and the metal–nitrogen σ-bonding orbitals. The empty, higher lying orbitals that are most likely to interact are the metal $d\pi$ orbitals.

Table II. Average Nitrogen Lone-Pair Ionization Potentials and the Corresponding Localized Orbital Ionization Potentials (eV) for Transition-Metal Dimethylamido Complexes

compd	COG, N lone-pair IP[a]	LOIP[b] (N 2p)	IP – LOIP
$Ti[N(CH_3)_2]_4$	7.56	7.9_0	−0.3
$Zr[N(CH_3)_2]_4$	7.71	8.1_3	−0.4
$Hf[N(CH_3)_2]_4$	7.93	8.1_1	−0.2
$Nb[N(CH_3)_2]_5$	7.51	7.9_8	−0.5
$Ta[N(CH_3)_2]_5$	7.65	8.0_6	−0.4
$Mo[N(CH_3)_2]_4$	7.85	8.0_7	−0.2
$W[N(CH_3)_2]_6$	7.33	7.7_2	−0.4

[a] Center of gravity of nitrogen lone-pair IPs. Data from ref 8 and 9. [b] Calculated with the N 1s and lone-pair ionization potentials for planar ammonia, 405.3 and 9.8 eV, respectively.[7]

From Table II we see that all the COG – LOIP values are negative. These data show that the repulsive interactions outweigh the $p\pi \rightarrow d\pi$ interactions. A lower limit to the lone-pair–CH_3 interaction energy can be obtained from the data for trimethylamine.[7] In trimethylamine, the nitrogen lone pair has a net destabilization of 0.9 eV. This value may be equated to the difference between the lone-pair–CH_3 destabilization energy and the stabilization of the lone pair due to N–C bonding. Thus the actual lone-pair–CH_3 destabilization energy in trimethylamine is greater than 0.9 eV. For the planar $-N(CH_3)_2$ group, the destabilization energy would be expected to be reduced by a factor of $^2/_3$ because of the reduction in the number of CH_3 groups but to be increased because of the better orbital overlap in the planar configuration. Hence one predicts that the destabilization of the lone pairs due to interactions with the CH_3 groups in the metal amides is considerably greater than 0.6 eV. Because all of the COG – LOIP values in Table II are less negative than 0.6 eV, we conclude that all of the metal amide lone pairs are significantly stabilized by $p\pi \rightarrow d\pi$ bonding.

To whatever extent the lone pairs are destabilized by repulsions of metal–nitrogen σ-bonding orbitals, the calculated $p\pi \rightarrow d\pi$ stabilization energies are greater. Only in the case of $W[N(CH_3)_2]_6$ can we draw any quantitative conclusions about such repulsions. The second ionization potential of $W[N(CH_3)_2]_6$, 7.92 eV,[8] corresponds to a lone-pair orbital of t_g symmetry. Because there is no W–N σ-bonding orbital of this symmetry, this orbital (relative to the LOIP) is unaffected by repulsions by W–N σ-bonding electrons. The 0.2-eV stabilization energy (relative to

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(10) The LOIP is the lone pair ionization potential of planar ammonia plus eight-tenths of the difference between the N is binding energies of the metal amide and planar ammonia.

the LOIP) is the net result of more than 0.6-eV destabilization by CH_3 group repulsion and more than 0.8-eV stabilization by $p\pi \rightarrow d\pi$ stabilization.

The first ionization potential of $W[N(CH_3)_2]_6$, 6.74 eV,[8] corresponds to a lone-pair orbital of t_u symmetry. This orbital cannot engage in $p\pi \rightarrow d\pi$ bonding, but it can be destabilized by interaction with the lower lying (IP = 9.55 eV) W–N σ-bonding orbital of the same symmetry. The 1.2-eV decrease in ionization potential on going from the t_g orbital to the t_u orbital is due to the loss of $p\pi \rightarrow d\pi$ bonding and, possibly, to W–N σ-bonding repulsions. Because the $p\pi \rightarrow d\pi$ stabilization is greater than 0.8 eV, the W–N σ-bond destabilization must be less than about 0.4 eV. In any event, it is clear that the $p\pi \rightarrow d\pi$ stabilization energy of the t_g lone pairs in $W[N(CH_3)_2]_6$ must lie in the range 0.8–1.2 eV.

Unfortunately, the situation in the four-coordinate dimethylamide complexes is not as straightforward. These complexes possess D_{2d} symmetry, and both the lone-pair and M–N σ-bonding orbitals belong to the same representations (e, b_2, and a_1). Therefore, all of the lone-pair orbitals will be destabilized by M–N σ-bond repulsions because they lie higher in energy than the σ-bonding orbitals. Although the gas-phase structures of the five-coordinate species are unknown, it is probable from the number of bands in the valence spectrum that their molecular symmetry is no higher than C_{2v}, so that interaction of the lone-pair and σ-bonding orbitals would also be expected.

The situation in these compounds is analogous to that in ONF_3, where the lone pairs of the oxygen atom undergo only a slight net destabilization because of approximately equal interactions with the N–F σ-bonding orbitals and the N–F σ^*-antibonding orbitals.[11] A related situation is found in BH_3CO, where the 5σ orbital of CO is only slightly stabilized on coordination to the BH_3 group (probably because of approximately equal interactions with the BH_3 "acceptor" orbital and the B 2s orbital).[12]

Thus, although the data do not allow an exact determination of the lone-pair stabilization due to π-donor bonding, they do indicate that such bonding occurs in these compounds and that the traditional rationalization of the structural data is reasonable.

Experimental Section

All manipulations were performed under nitrogen. The titanium, zirconium, and hafnium amides were prepared by a literature method[13] except that hexane was used as the reaction solvent and the mixtures of $LiN(CH_3)_2$ and $TiCl_4$ or $ZrCl_4$ were refluxed for 8 h. In the case of the hafnium amide, diethyl ether was used as reaction solvent and the reaction time was 24 h. The niobium,[14] tantalum,[15] molybdenum,[16] and tungsten[17] amides were prepared by literature methods. All compounds were characterized by infrared spectroscopy,[18] and they gave molecular ions in their mass spectra. The liquid amide $Ti[N(CH_3)_2]_4$ was purified by distillation under reduced pressure, and the other solid amides were purified by crystallization from pentane followed by vacuum sublimation.

Gas-phase X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA 36 spectrometer equipped with a Mg anode. Spectra were collected with a repetitive scanning technique with periodic drift correction described elsewhere.[19,20] Spectra were calibrated against N_2 1s, Ne 1s, and Ne 2s reference peaks. The titanium, zirconium, and hafnium complexes were sufficiently volatile that they could be sublimed directly into the spectrometer gas cell through large diameter (1.5-cm) tubing from an external sample reservoir. Flow was controlled by cooling the sample reservoir.

The tungsten, niobium, and tantalum complexes were volatilized in a resistively heated gas cell of our own design.[21] To prevent hydrolysis, the samples were loaded in thin-walled glass bulbs in an inert-atmosphere dry-box and the bulbs were sealed on the vacuum line and crushed in the gas cell after the spectrometer was pumped below 4×10^{-7} torr. The spectra were obtained at the following gas cell temperatures: $W[N(CH_3)_2]_6$, 88 °C; $Nb[N(CH_3)_2]_5$, 42 °C; $Ta[N(CH_3)_2]_5$, 47 °C.

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