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Correlation between N 1s XPS Binding Energy and Bond Distance in Metal Amido, Imido, and Nitrido Complexes

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Synchrotron-based X-ray photoelectron spectroscopy is used to measure N 1s binding energies of several metal amido, imido, and nitrido complexes of group 5 and 6 metals. The N 1s binding energy decreases as the formal M–N bond order increases. A simple correlation between the contraction of the M–N bond and the lowering of binding energy is also observed. This correlation supports a notion that the bonding character of a linear metal–imido linkage resembles that of a metal–nitrido linkage closely.

Transitional metal−nitrogen complexes, encompassing multiple metal−nitrogen bonds like amido, imido, and nitrido, have been a focus of much research effort.[1−3] Fundamental studies have been undertaken to address issues such as chemical bonding, structure, and reactivity.[4] Meanwhile, many potential industrial applications have been explored in areas such as polymerization, metathesis, and thin film precursors.[5−7] On the basis of simple Lewis concept, metal−amido (M−N), metal−imido (M=N), and metal−nitrido (M≡N) bonds can be assigned with formal bond orders of 1−3, respectively, and bond distances, a manifestation of bond strength, are expected to vary accordingly. However, M−N bonding interaction is more complex than just described and bond order concept may not be used without any ambiguity. For instance, the M−N bond in metal−amido complexes is shortened with the inclusion of π-bonding interaction; the bond distances in the metal−imido complexes can vary between those for double bond and triple bond, depending on whether the bond is “bent” or “linear”.[1,2,8]

There exist several techniques capable of providing experimental estimates of metal−ligand bonding character in inorganic chemistry. For instance, the orbital mixing of the ligand and metal can be probed via spectroscopic methods such as ligand K-edge X-ray absorption spectroscopy[9] and core level X-ray photoelectron spectroscopy (XPS).[10] In XPS, the binding energy (b.e.) shift of a core level, within the simple charge potential model that neglects final state relaxation, provides an estimate of local charge located on the atom,[11] which depends sensitively on oxidation state, molecular environment, etc. Previous XPS core level shift studies of metal complexes focused on the metal centers exclusively and have addressed the issue of the applicability of ligand group shift[12] and the feasibility of using XPS to assign oxidation state to poorly understood electronic interaction in molybdenum−pterin heterocycles.[13]

Here we would like to present a correlation found between metal−ligand bond distance and XPS b.e. of the ligand in metal complexes. Specifically, we have studied the variation of N 1s b.e. for metal complexes that include $Ta(NEtMe)_5$[14a] (**a**), t-BuN=$Ta(CH_2Bu$-$t)_3$[14b] (**b**), t-BuN=$Ta(NEtMe)_3$[14c] (**c**),

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t-BuN═Ta(NEt$_2$)$_3$[14d] (**d**), (*t*-BuN═)$_2$W(NHBu-*t*)$_2$[14e] (**e**), and N≡Cr(OBu-*t*)$_3$[14f] (**f**). A successful recast of N 1s b.e. dependence on loosely grounded bond order concept into a dependence on M−N bond distance underlines the importance of ligand charge in determining the overall M−N bonding interaction in metal complexes.

The XPS data for the metal complexes were acquired with the complexes adsorbed on a Cu(111) surface at 300 K to eliminate charging problems associated with bulk materials. The binding energy scale is conveniently referenced to Fermi level of Cu substrate. Clean Cu(111) was prepared by sputtering and annealing. The complex enclosed in a glass vial was admitted into the UHV chamber via a variable leak valve. The intact adsorption of metal complex could only be achieved after the gas manifold was thoroughly passivated.[15] The inert Cu(111) surface in conjunction with the bulky nature of the metal complexes is believed to lessen the electronic perturbation of the metal complexes by substrate surface significantly.[16] Synchrotron-based XPS (SR-XPS) offers particular advantages of higher photoemission cross section and better energy resolution than available with conventional XPS technique[17] and the XPS data were acquired at the wide-range spherical grating monochromator beamline of NSRRC. A combined instrumental resolution, including the beamline and energy analyzer, was estimated to be better than 0.3 eV for the 600 eV photons used here.

Figure 1 presents the N 1s SR-XPS spectra for all the metal complexes reported here. A single peak at a b.e. of 398.2 eV is found for the complex **a**, as shown in Figure 1a, in good agreement with previous XPS measurement of 398.4 eV for Ti(NMe$_2$)$_4$ complex.[18] The complex **b** with only one imido ligand attached to a Ta metal center exhibits a single N 1s peak at 397.2 eV, shown in Figure 1b. The complex **c**, having three amido and one imido ligands, exhibits two well-resolved peaks at 398.0 and 396.8 eV accordingly, as shown in Figure 1c. The integrated peak ratio of 3:1 is consistent with the stoichiometry ratio for two types of N atoms. The complex **d**, a slight variant of the complex **c**, also exhibits two N 1s peaks at 397.9 and 396.8 eV of the expected intensity ratio. A further increase in the number of imido groups forms a W complex of **e**, containing two amido and two imido groups, and its N 1s XPS spectrum is shown in Figure 1e. Peak fitting reveals two peaks at the b.e. of 398.7 and 397.3 eV, shifted toward higher b.e. by 0.8 and 0.5 eV, respectively, as compared with the corresponding ligands in the Ta metal complexes, **c** and **d**. The shift toward higher b.e. is consistent with a larger Pauling electronegativity for W (2.36) than for Ta (1.5). The complex **e** is thermally labile at room temperature, and the amido group decomposes via a α-hydrogen abstraction pathway to imido.[19] As a result, peak intensity ratio departs from the expected 1:1 ratio and more signal is found for imido at the lower b.e. side.

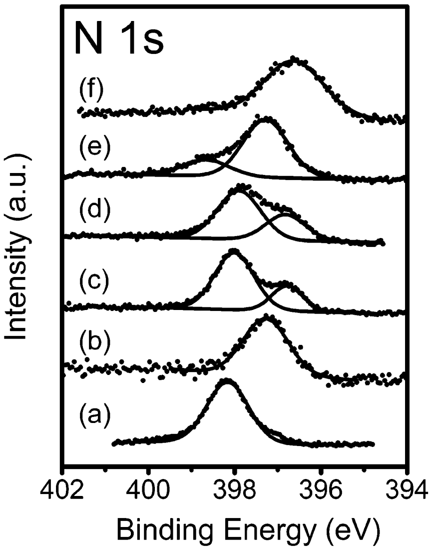

Figure 1. N 1s SR-XPS for 1 L of complexes adsorbed on Cu(111) surface at 300 K. (a) Ta(NEtMe)$_5$, (b) *t*-BuN═Ta(CH$_2$Bu-*t*)$_3$, (c) *t*-BuN═Ta-(NEtMe)$_3$, (d) *t*-BuN═Ta(NEt$_2$)$_3$, (e) (*t*-BuN═)$_2$W(NHBu-*t*)$_2$, and (f) N≡Cr(OBu-*t*)$_3$.

Table 1. The Selected b.e. (eV) and Formal Bond Orders of **a**−**f**

complex	M−N bond order	binding energy (eV) N 1s	metal
Ta(NEtMe)$_5$, **a**	Ta−N	398.2	24.0 (Ta 4f$_{7/2}$)
t-BuN═Ta(CH$_2$Bu-*t*)$_3$, **b**	Ta═N	397.2	23.5 (Ta 4f$_{7/2}$)
t-BuN═Ta(NEtMe)$_3$, **c**	Ta−N	398.0	23.9 (Ta 4f$_{7/2}$)
	Ta═N	396.8	
t-BuN═Ta(NEt$_2$)$_3$, **d**	Ta−N	397.9	23.9 (Ta 4f$_{7/2}$)
	Ta═N	396.8	
(*t*-BuN═)$_2$W(NHBu-*t*)$_2$, **e**	W−N	398.7	33.5 (W 4f$_{7/2}$)
	W═N	397.3	
N≡Cr(OBu-*t*)$_3$, **f**	Cr≡N	396.6	575.2 (Cr 2p$_{3/2}$)

Last, the N 1s peak for the nitrido complex **f** is shown in Figure 1f. A single peak at 396.6 eV is observed for nitrido bonded to Cr metal. This b.e. value is only slightly less than those of imido groups bonded to Ta (396.8 eV) and W (397.3 eV). It is noted that the b.e. values of the metals in the metal complexes are always higher than those of the corresponding metals, owing to the higher metal oxidation states in the complexes. The observed b.e. values for both N 1s and metal core levels together with formal bond orders for the chemical bonds between M and N atoms are compiled in Table 1. Metal core levels seem to be relatively insensitive to the change of M−N bond order. For instance, in **a**, **c**, and **d** complexes, Ta 4f$_{7/2}$ remains at ∼24.0 eV despite a significant variation of N 1s b.e. of the ligands.

The observed N 1s b.e. values for various metal complexes follow a general trend: b.e.$_{\text{amido}}$ > b.e.$_{\text{imido}}$ > b.e.$_{\text{nitrido}}$. It is

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(15) The complex was dosed via an effusive doser. The effusive source used was a 3.2-mm-diameter glass tube bearing a 500-μm pinhole. The gas manifold was constructed from glass as much as possible to minimize the likely precursor decomposition on metallic parts during the transfer to the substrate. Passivation was done by continuously running the vapor of the complex through the passage in the gas manifold. Being able to observe a well-defined, single-component metal XPS peak for the metal complex adsorbed on a cold substrate constitutes a proof for a complete passivation.

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Table 2. Selected M−N Bond Distances (Å) and χ Values (Å)

	Ta−N	Ta=N		W−N	W=N	Cr≡N
M−N	1.99(1)[21]	1.784(1)[14b]	1.77(2)[21]	1.975(4)[22]	1.740(4)[22]	1.538(5)[14f]
χ	0.10	0.31	0.32	0.08	0.31	0.39

tempting to explain the trend using simple formal charge concept. The formal charge assigned to the N atoms for the amido, imido, and nitrido ligands are −1, −2, and −3, respectively. Assuming a similar relaxation effect for N atoms in the ligands, an increasingly negative formal charge at the nitrogen atom is then associated with a smaller N 1s b.e. straightforwardly. Unfortunately, the formal charge is derived from an oversimplified concept that does not truly reflect the charge distribution as the M−N multiple bond is formed. The molecular orbital bonding picture indicates that the N atom of the ligands, often known as π-donors, contributes more to the M−N bonding orbitals than the metal atom does.[20] Is it possible to assess the b.e. variation of N 1s core levels within the framework of molecular bonding in M−N bonds? To begin with, by recognizing that altering bonding interaction manifests itself in a change of M−N bond distance, we define a parameter χ that describes how the M−N bond gets shortened relative to the sum of the free atom values as the M−N bond is developed.

$$\chi = (r_M + r_N) - R_{M-N} \qquad (1)$$

Here, r_M and r_N are the bonding radii of M and N. R_{M-N} is the M−N bond distance calculated from the crystallographic data. The data used to derive χ are listed in Table 2.

A plot of the observed N 1s b.e. vs χ parameter is presented in Figure 2. A better correlated, approximately linear relationship is found for all complexes. Particular noteworthy is the nitrido datum that is now more in line with other data. The trend of decreasing N 1s b.e. for the increasing χ values is consistent with the ligand−metal charge-transfer bonding picture. When a M−N multiple bond is formed, more valence electrons from both M and N atoms are involved in bonding to form a shortened M−N bond. Due to this bond shortening, the charge density around the N atom moves closer to the nitrogen nucleus. As a result, a photoionized N 1s core electron will experience more screening due to the inward contraction of valence electrons, thereby resulting in a smaller b.e. of the N 1s core level. Figure 2 also suggests that the M−imido bonding character of **b**−**e** is comparable to that of M−nitrido, **f**. This supports the use of $M\overset{\leftarrow}{=}NR$, instead of $M{=}NR$, as the notation for a linear metal imido bond.

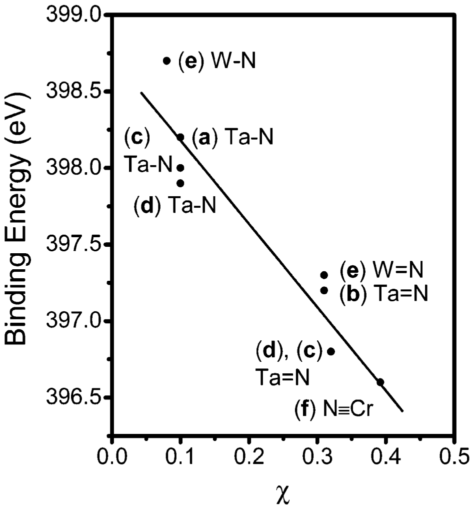

Figure 2. Correlation of N 1s b.e. to χ parameter. Straight line is a guide to eyes.

In summary, based on high-resolution XPS data obtained for a series of metal−nitrogen complexes, the observed N 1s b.e. values are found to correlate better with the corresponding M−N bond distance than with somewhat problematic bond-order parameters. More extension of this concept to other systems is in progress.

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