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Nitrogen 1s Binding Energies of Some Azide, Dinitrogen and Nitride Complexes of Transition Metals

by Patricia Finn and William L. Jolly

We have used X-ray photoelectron spectroscopy to determine the nitrogen 1s binding energies of azide, dinitrogen, and nitride complexes of several transition metals. Such data are of interest because the binding energy shifts can be interpreted in terms of the interaction of the ligands with the transition metal atoms.

Experimental

The compounds $Ni(N_3)(NO)[P(C_6H_5)_3]_2$,[1] trans-$[Ru(N_3)Cl(diars)_2]$,[2] trans-$[Co(N_3)_2(diars)_2]ClO_4$,[2] trans-$[Ru(N_2)Cl(diars)_2]$,[2] and $[C_6H_5(N_2)]BF_4$[3] were kindly supplied by Philip G. Douglas and Robert D. Feltham of the University of Arizona. We prepared $\{Cu(N_3)[P(C_6H_5)_3]_2\}_2$,[4] $[Rh(N_3)(CO)_2]_2$,[5] $[As(C_6H_5)_4]_2[Fe(N_3)_5]$,[6] $K_3[Ru_2N(Cl)_8(H_2O)_2]$,[7] and $ReN(Cl)_2[P(C_6H_5)_3]_2$[8] by known procedures. The KBr pellet infrared spectra of these complexes were in good agreement with the literature data.

The powdered samples were brushed onto double-faced conducting tape attached to an aluminum plate. In each case, the carbon 1s line (due to a film of pump oil on the samples) was recorded and used as a reference peak. Individual lines had widths of 1.4-2.6 eV. The kinetic energy of the photoelectron, E_K, was measured in an iron-free double-focusing magnetic spectrometer[9] in which the incident radiation, $E_{h\nu}$, was magnesium K_α

X-radiation (1253.6 eV) and for which the work function, ϕ_s, was taken as 4.0 eV. The nitrogen 1s binding energy, E_B, (the difference between the Fermi energy and the 1s atomic energy) was calculated from the relation $E_B = E_{h\nu} - E_K - \phi_s$.

Results

The data are presented in Table I.

Azide Complexes.- The first group of compounds in Table I contain azide ions in various environments. It is noteworthy that sodium azide and the azide complexes have very similar spectra, with two peaks separated by 4.3 ± 0.4 eV. The peak at lower binding energy (corresponding to the two end atoms) has twice the intensity of the other peak (corresponding to the middle atom). These results indicate that the internal bonding of the azide ion is essentially unaffected by coordination to a transition metal atom; that is, the azide ion appears to be linked to the metal atom by an ionic bond with little polarization. The infrared spectra and X-ray diffraction structural data of such compounds are consistent with these conclusions. Thus the asymmetric stretching frequency and the bending frequency of the azide ion in complexes are almost unchanged from those of the azide ion in sodium azide.[1,2,4-6] The N-N bond distances in azide complexes are within 0.02 Å of that in sodium azide.[10-12]

Both peaks of $[As(C_6H_5)_4]_2[Fe(N_3)_5]$, the only anionic azide complex considered, are appreciably shifted to lower binding energies (by 0.6 and 0.9 eV) from the peaks of sodium azide. Probably the -2 charge on the anion is responsible for the lower binding energies.

Dinitrogen Complexes.- The Ru-N bond length of 1.894 Å for the N_2 group in $[Ru(N_3)(N_2)(en)_2]$[13] is significantly shorter than the Ru-N single bond distance of 2.144 Å in $[Ru(NH_3)_6]I_2$.[14] Similar evidence for partial multiple bond character in metal-N_2 bonds is found for other transition metal complexes.[15-18] Thus a dinitrogen complex can be considered to be a hybrid of two major resonance forms, $M - \overset{+}{N} = N$ and $M = \overset{+}{N} = \overset{-}{N}$. Because the nitrogen atom directly attached to the metal atom has a formal positive charge in both forms, we expect decreased electron density on this nitrogen atom and a correspondingly higher binding energy. The nitrogen 1s spectrum of trans-$[Ru(N_2)Cl(diars)_2]$ consists of two peaks; we assign the higher binding energy to the nitrogen atom directly attached to the ruthenium atom. Leigh et al.[19] made a similar assignment for $[Re(N_2)Cl(diphos)_2]$.

We found two nitrogen 1s peaks for $[C_6H_5(N_2)]BF_4$, with a peak separation of the same order of magnitude (1.3 eV) as found for the transition metal compounds. However, both peaks are at higher binding energy probably because of the +1 charge of the diazonium ion. For all resonance forms the nitrogen atom directly attached to the phenyl group has a formal positive charge; therefore the higher binding energy peak is assigned to this nitrogen atom.

Nitride Complexes.- The nitrogen 1s binding energies of $K_3[Ru_2N(Cl)_8(H_2O)_2]$ and $ReN(Cl)_2[P(C_6H_5)_3]_2$ are of interest because these complexes contain nitride ion ligands which are bridging and non-bridging, respectively. In the former complex, two metal atoms compete for the electron density of the bridging nitride, therefore a higher binding energy is observed for this compound even though the complex has a -3 charge.

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Table I

The Nitrogen 1s Binding Energies of Some Transition Metal Complexes

Compound	Nitrogen 1s Binding Energy (eV)	Intensity Ratio	Separation (eV)
NaN_3	403.7, 399.3[a]	1:2	4.4
$Ni(N_3)(NO)[P(C_6H_5)_3]_2$	403.8, 399.6	1:2	4.2
trans-$[Ru(N_3)Cl(diars)_2]$	403.9, 399.2	1:2	4.7
trans-$[Co(N_3)_2(diars)_2]ClO_4$	403.2, 399.1	1:2	4.1
$\{Cu(N_3)[P(C_6H_5)_3]_2\}_2$	403.7, 399.2	1:2	4.5
$[Rh(N_3)(CO)_2]_2$	403.2, 399.3	1:2	3.9
$[As(C_6H_5)_4]_2[Fe(N_3)_5]$	402.8, 398.7	1:2	4.1
trans-$[Ru(N_2)Cl(diars)_2]$	402.3, 400.7	1:1	1.6
$Re(N_2)Cl(diphos)_2$	399.9, 397.9[b]	1:1	2.0
$[C_6H_5(N_2)]BF_4$	405.1, 403.8	1:1	1.3
$K_3[Ru_2N(Cl)_8(H_2O)_2]$	399.8		
$ReN(Cl)_2[P(C_6H_5)_3]_2$	398.8		

[a] D. Hendrickson, J. M. Hollander and W. L. Jolly, Inorg. Chem., 8, 2642 (1969).

[b] See reference 19.

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