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Notes

Formal Oxidation States vs π-Effects in Isostructural Low-Symmetry $[MoNO]^{3+}$ and $[MoO]^{3+}$ Complexes: A Photoelectron Spectroscopy Study

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Introduction

There have been few direct experimental comparisons of the differing π-interactions of a terminal oxo group and a nitrosyl group. Over the past 15 years, numerous LMo(E)(X,Y) compounds (L = hydrotris(3,5-dimethylpyrazolyl)borate; E = O, NO; X, Y = halide, alkoxide, thiolate, amide) have been prepared.[1,2] These complexes provide an excellent opportunity to directly compare the electronic and spectroscopic properties of the $[MoNO]^{3+}$ and $[MoO]^{3+}$ fragments in isostructural complexes in which all the remaining coordinating ligands are identical. The formal oxidation states of the molybdenum atom in these two families of complexes differ. The linear diamagnetic $[MoNO]^{3+}$ fragment is often described as $[Mo^{II}(NO)^{+}]^{3+}$, which contrasts with the paramagnetic $[Mo^{V}O]^{3+}$ description. However, the $[MoNO]^{3+}$ complexes undergo facile one-electron *reduction* to give complexes whose EPR spectra[3,4] are similar to those of neutral LMo(O)(X,Y) complexes.[5]

Gas-phase photoelectron spectroscopy (PES) affords information about the orbital ionization energies of valence electrons free from the complications of solvent or solid-state perturbations. Comparison of spectra from structurally related complexes can give insight into secondary effects which affect the electron distribution and binding energies in a given compound.[6] Previously, we reported PES spectra for a series of bis(alkoxide) complexes of the form $LMo(O)(OR)_2$.[7] Here we compare the PES of such $LMoO(OR)_2$ complexes to that the isostructural analogues $LMo(NO)(OR)_2$.

Experimental Section

Preparation. The $LMo(O)(OEt)_2$ complex was prepared by literature methods, with the potassium salt of L prepared according to the method of Trofimenko,[8] and characterized by mass spectrometry, IR spectroscopy, and UV−visible spectroscopy.[2] The nitrosyl complexes were provided by Dr. Chris J. Jones of the University of Birmingham, England, and were prepared by literature methods.[3]

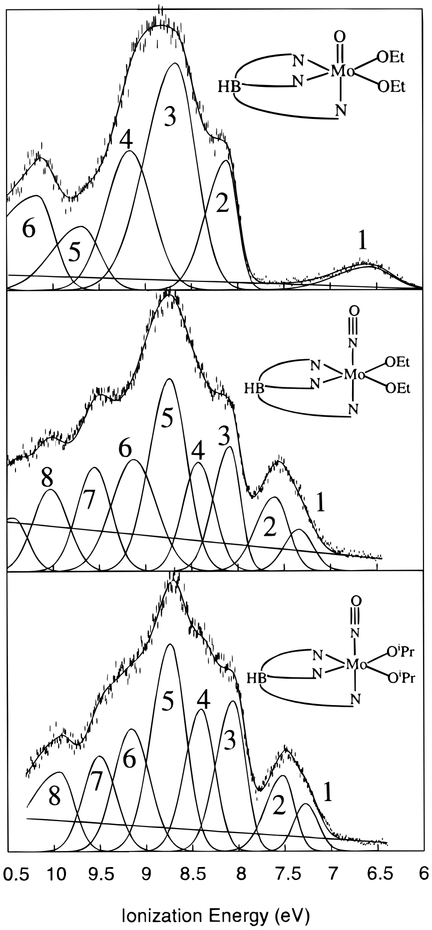

Figure 1. He I PES spectra of $LMo(E)(OR)_2$ complexes. For E = O (top spectrum) band 1 is the metal-based ionization; for E = NO (lower two spectra) bands 1 and 2 are metal-based ionizations. The spectral features at energies ≥8 eV are due to ligand-based ionizations.

Photoelectron Spectra. All PES spectra were measured using a modified GCA-McPherson ESCA 36 spectrometer with a 36 cm radius hemispherical analyzer (8 cm gap) and customized sample cells, excitation sources, detection control, and data collections methods.[9] The ionization energy scale was calibrated using the $^2E_{1/2}$ (9.538 eV) ionization of methyl iodide, with the Ar $^2P_{3/2}$ ionization (15.759 eV) used as an internal energy scale lock during data collection. The He I spectrum of each compound was collected at least twice. The spectra from each collection were identical, and no decomposition was observed in either the PES spectrum or the mass spectra in the gas phase or as a solid residue. The sublimation temperature ranges for the data collections measured using a K type thermocouple passed through a vacuum feed attached to the sample cell were as follows: 116−124 °C for $LMo(O)(OEt)_2$, 112−120 °C for $LMo(NO)(OEt)_2$, and 112−120 °C for $LMo(NO)(O^iPr)_2$. The data were fit analytically with asymmetric Gaussians using the program Fp,[10] with a confidence limit of peak positions and width deviations generally considered as ±0.02 eV.

Results and Discussion

Figure 1 shows the He I PES spectra for the three $LMo(O,NO)(OR)_2$ complexes. The spectral features and Gauss-

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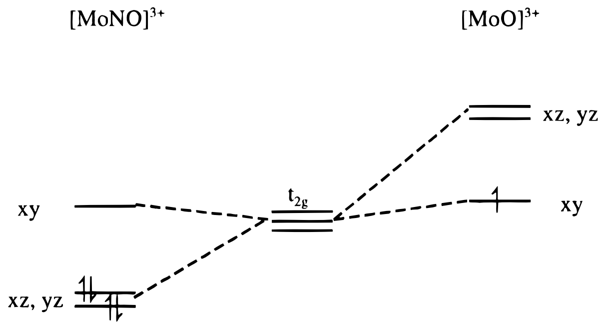

Figure 2. Splitting diagram for the metal t_{2g} orbitals for the $[MoNO]^{3+}$ (left) and $[MoO]^{3+}$ (right) cases.

ian fits for $LMo(O)(OEt)_2$ are identical within experimental error to those reported previously.[7] The first band at 6.57 eV is attributed to the ionization of the Mo d^1 electron, with the remaining "forest region" due primarily to ionizations from the ligand L. The spectral features for the two NO complexes of Figure 1 are similar to one another, with both exhibiting a first ionization at ∼7.5 eV. This first spectral feature is best fit by two asymmetric Gaussians and is attributed to ionizations from the two nearly degenerate orbitals which are Mo(d) and NO(π*) in character. The splitting of these orbitals can be attributed to the C_s symmetry of the molecules. The rest of each spectrum is attributed to ligand-based ionizations. The ligand-based ionizations for both $LMoO(OEt)_2$ and $LMo(NO)(OR)_2$ are quite similar and are discussed eleswhere.[11]

The relative positions of the metal-based ionizations are of particular interest because the general assumption is that transition metal complexes in high oxidation states are more difficult to ionize than those in lower oxidation states. The oxo complex of Figure 1 is formally Mo(V), whereas the nitrosyl complexes are formally Mo(II). Formal oxidation state arguments would predict that the Mo(V) oxo complex should be more difficult to ionize. However, the *opposite* behavior is observed; the formally d^1 Mo(V) oxo complex is ∼0.8 eV *easier* to ionize than the formally d^4 Mo(II) analogues.

A molecular orbital description of similar complexes has been reported by Bursten and Cayton, who compared the splitting of the t_{2g} orbitals of transition metal centers upon interactions with NO and oxo groups.[12] For the present complexes, the interaction of the π*(NO) orbitals with these metal d orbitals stabilizes the filled d_{xz} and d_{yz} orbitals; the d_{xy} is empty and nonbonding with respect to the MoNO unit. However, in the case of an oxo donor, the nonbonding d_{xy} is the HOMO because the d_{xz} and d_{yz} orbitals are strongly *antibonding* due to their interaction with the filled oxo π orbital (Figure 2). The PES data of Figure 1 corroborate this description, showing that the d_{xz} and d_{yz} orbitals in the NO complexes are substantially stabilized relative to the singly-occupied nonbonding d_{xy} orbital of $LMo(O)(OR)_2$.

These PES studies have allowed direct experimental comparison of the π effects that oxo and nitrosyl ligands have on a metal center and show that the strong π-interactions of oxo and nitrosyl groups lead to a breakdown of simple formal oxidation state arguments. The π-accepting ability of the NO ligand makes the formally Mo(II) complexes ∼0.8 eV *more difficult* to ionize than the formally Mo(V) oxo analogues. These results are in stark contrast to the behavior predicted from formal oxidation state considerations.

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