Inorg. Chem. **2002**, *41*, 5907–5911

Inorganic Chemistry
Article

Photoelectron Spectroscopy of Bis(2,4-Pentanedione)–Oxovanadium(IV) [VO(acac)$_2$] and Derivatives: Substituent Effects on the 2,4-Pentanedione Donor

Nadine E. Gruhn,[‡] Laura J. Michelsen,[†] and Barry L. Westcott*,[†]

Department of Chemistry, Central Connecticut State University, New Britain, Connecticut 06050,
and The Center for Gas-Phase Electron Spectroscopy, Department of Chemistry,
The University of Arizona, Tucson, Arizona 85721

Received March 19, 2002

The electronic structure of derivatives of VO(acac)$_2$ is probed using gas-phase UV-photoelectron spectroscopy [acac = 2,4-pentanedione]. The effect on the metal center of electron-donating and -withdrawing groups on the acac ligands is examined. Ionizations from metal-based, acac-based, and V═O-based orbitals are clearly observed. We find that changes at the ligand periphery lead to equivalent changes in the energies of the metal-based and ligand-based ionizations. Additionally, we find that a linear correlation exists between the ionization energies of the metalated complexes and the pK_a values of the free ligands, indicating that the pK_a is a good indication of the overall electron-donating abilities of acac ligands.

Introduction

The chemistry of vanadium has received renewed interest in recent years because of vanadium's role in many environmental and biological processes.[1−6] Vanadium oxide (vanadyl) complexes, in particular, have come under close scrutiny because of their utility as insulin mimetics.[1] In order to develop a better understanding of the electronic structure of vanadium complexes, including those that are biologically relevant, we are studying the effects that changes to the ligand periphery have on the electronic structure at the metal center. Our primary method of studying electronic structure is photoelectron spectroscopy.

Photoelectron spectroscopy has proven a useful technique for quantitatively measuring the effects that chemical substituents have upon the electronic structure and charge potentials of both organic[2] and transition-metal-containing molecules.[3] The comparison of the photoelectron spectra of similar molecules shows how much ionizations are shifted by chemical substituents. In the orbital model of electronic structure, these shifts in ionizations can be correlated to the amount of stabilization of molecular orbitals caused by electron-withdrawing substituents, or destabilization of molecular orbitals caused by electron-donating substituents. Photoelectron spectroscopy offers particularly valuable information because ionizations from orbitals localized at different locations within a molecule can often be used to probe the effects of chemical substituents throughout the molecular framework. For example, it has typically been found for transition-metal-containing molecules that, perhaps as expected, ligand substituents will perturb the molecular electronic structure close to the site of the substituent more than it will perturb the molecular electronic structure at remote parts of the molecule.[9−13]

---

* Author to whom correspondence should be addressed. E-mail: westcottb@ccsu.edu.

[†] Central Connecticut State University.

[‡] The University of Arizona.

(1) Crans, D. C. *J. Inorg. Biochem.* **2000**, *80*, 123−131.
(2) Arber, J. M.; de Boer, E.; Garner, C. D.; Hansain, S. S.; Wever, R. *Biochemistry* **1989**, *28*, 7678.
(3) Carrano, C. J.; Mohan, M.; Holmes, S. M.; de la Rosa, R.; Butler, A.; Charnock, J. M.; Garner, C. D. *Inorg. Chem.* **1994**, *33*, 646.
(4) Winter, G. E. M.; Butler, A. *Biochemistry* **1996**, *35*, 11805.
(5) Ryan, D. E.; Grant, K. B.; Nakanishi, K.; Frank, P.; Hodgson, K. O. *Biochemistry* **1996**, *35*, 8651.
(6) Bayer, E. *Metal Ions Biol. Syst.* **1995**, *31*, 407.
(7) Crans, D. C. *J. Inorg. Biochem.* **2000**, *80*, 123−131.
(8) Potts, A. W.; Price, W. C.; Streets, D. G.; Williams, T. A. *Faraday Dicuss. Chem. Soc.* **1972**, 168−181.
(9) Green, J. C. *Acc. Chem. Res.* **1994**, *27*, 131−137.
(10) Lichtenberger, D. L.; Rai-Chaudhuri, A. *Organometallics* **1990**, *9*, 1686−1690.
(11) Calabro, D. C.; Hubbard, J. L.; Blevins, D. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839.
(12) Lichtenberger, D. L.; Calabro, D. C.; Kellog, G. E. *Organometallics* **1984**, *3*, 1623.
(13) Lichtenberger, D. L.; Elkadi, Y.; Gruhn, N. E.; Hughes, P. P.; Curnow, O. J.; Zheng, X. *Organometallics* **1997**, *16*, 5209.

10.1021/ic0256056 CCC: $22.00

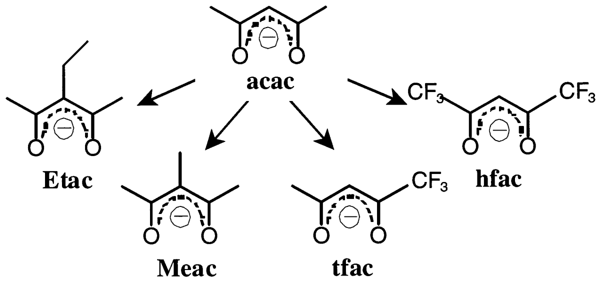

Figure 1. Structures of the ligands.

For this study attention was focused on the photoelectron spectroscopy of VO(acac)$_2$, where acac is 2,4-pentanedione, and analogous complexes with the substituted acac ligands tfac (1,1,1-trifluoro-2,4-pentanedione), hfac (1,1,1,5,5,5-hexafluoro-2,4-pentanedione), etac (3-ethyl-2,4-pentanedione), and meac (3-methyl-2,4-pentanedione) (Figure 1). Our choice of this series of compounds for study is based on three points. First, as previously mentioned, VO(acac)$_2$ and derivatives, including those studied here, have shown insulin mimetic capabilities in studies on rats.[14] Second, the chemistry, structure, and spectroscopy of acac complexes are well established.[15,16] Third, additional background information is available because the photoelectron spectrum of VO(acac)$_2$ has previously been reported.[17]

The goals of this study are to investigate what effect the acac ligand substituents have upon the overall donor ability of these ligands, and to see how well the relative donor abilities compare to other properties often used to predict donor ability, such as the pK_a of the conjugate acid of these acac ligands. The photoelectron spectra of these molecules are convenient probes for analyzing how the electronic structure throughout the molecules is affected by the substituents, because ionizations from orbitals primarily associated with the oxo lone pairs, metal d orbitals, and acac ligand-based orbitals are all clearly observed and identified. While the photoelectron spectra of many homoleptic acac complexes have been reported,[18−21] these molecules have not been as useful as these vanadyl complexes for studying the donor abilities of the acac ligands because the metal-based ionizations are typically obscured by the acac-based ionizations, and no other ancillary ligand ionizations are present. As will be shown, the relative donor abilities of these acac ligands as measured by the photoelectron spectroscopy of the metal complexes do correlate with the pK_a of the free ligands.

Experimental Section

Synthesis. VO(acac)$_2$ and all starting materials were used as received from Aldrich. VO(hfac)$_2$, VO(tfac)$_2$ VO(etac)$_2$, and VO(meac)$_2$ were prepared via published procedures.[22−24]

Data Collection. The HeI (21.2 eV) and HeII (40.8 eV) gas-phase photoelectron spectra were recorded using an instrument and general procedures that have been described previously.[25] The samples showed no signs of impurity or decomposition in the gas phase during controlled sublimation at 100−130 °C. A small amount of nonvolatile solid remained in the sample cell at the end of each experiment. During data collection the instrument resolution (measured using fwhm of the argon $^2P_{3/2}$ peak) was 0.015−0.020 eV for HeI and 0.022−0.026 eV for HeII.

Data Analysis. The spectra were fit analytically with asymmetric Gaussian peaks with a confidence limit of peak positions and width deviations generally considered as ± 0.02 eV ($\approx 3\sigma$ level).[26] For the different complexes, the HeI spectrum was fit first. The number of peaks used in each fit was based on the features of the band profile and the number of peaks necessary for a statistically good fit. For the HeII fits the peak positions and half-widths were fixed with respect to those of the HeI fit. Only the peak amplitudes were allowed to vary to account for changes in photoionization cross section.

Confidence limits for the relative integrated peak areas are about 5% with the primary source of uncertainty being the determination of the base line. The base line arises from electron scattering and is taken to be linear over the small energy range of these spectra. The fitting procedures used are described in more detail elsewhere.[25]

Computational Studies. Density functional molecular orbital calculations were performed on VO(acac)$_2$ using the Amsterdam Density Functional 2000 (ADF2000.01) package.[27−30] The molecular geometry was optimized at the GGA (BLYP) level with basis set IV (triple-ζ Slater-type orbitals plus polarization for all atoms). A frozen-core approximation was used with 1s−2p frozen on V and 1s frozen on C and O.

Results and Discussion

General Assignment of Spectra. The HeI spectra of all five complexes studied here are shown in Figure 2. All spectra show a similar pattern, with the primary difference among the spectra being that the peaks are shifted depending on the donating properties of the ligand (vide infra). Because the ground states of the neutral molecules are $S = {}^1/_2$ (V^{4+}, d^1, $^2A_1$), ionization from all the doubly occupied orbitals will lead to both singlet and triplet states due to exchange splitting between ligand and metal electrons. This splitting, however, appears to be insignificant for these complexes compared to the resolution of the experiment.

---

(14) Reul, B. A.; Amin, S. S.; Buchet, J.-P.; Ongemba, L. N.; Crans, D. C.; Bricjard, S. M. *Br. J. Pharmacol.* **1999**, *126*, 467−477.

(15) Mehrotra, R. C. *Pure Appl. Chem.* **1988**, *60*, 1349.

(16) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-diketones and Allied Derivatives*; Academic: London, 1978.

(17) Di Bella, S.; Lanza, G.; Gulino, A.; Fragalà, I. *Inorg. Chem.* **1996**, *35*, 3885−3890.

(18) Evans, S.; Hamnett, A.; Orchard, A. F.; Lloyd, D. R. *Faraday Discuss. Chem. Soc.* **1972**, 227−250.

(19) Westmore, J. B.; Reimer, M. L. J.; Reichert, C. *Can. J. Chem.* **1981**, *59*, 1797−1804.

(20) Vovna, V. I.; Lvov, I. B.; Slabzhennikov, S. N.; Ustinov, A. Y. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88−91*, 109−117.

(21) Brittain, H. G.; Disch, R. L. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *7*, 475−483.

(22) Felthouse, T. R.; Hendrickson, D. H. *Inorg. Chem.* **1978**, *17*, 2636.

(23) Carlin, R. L.; Walker, F. A. *J. Am. Chem. Soc.* **1965**, *87*, 2128.

(24) Amin, S. S.; Cryer, K.; Zhang, B.; Dutta, S. K.; Eaton, S. S.; Anderson, O. P.; Miller, S. M.; Reul, B. A.; Brichard, S. M.; Crans. D. C. *Inorg. Chem.* **2000**, *39*, 406−416.

(25) Westcott, B. L.; Gruhn, N. E.; Enemark, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 3382−3386 and references therein.

(26) Lichtenberger, D. L., Copenhaver, A. S. *J. Electron. Spectrosc. Relat. Phenom.* **1990**, *50*, 335.

(27) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1983**, *2*, 41.

(28) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.

(29) Bickelhaupt, F. M.; van Eikema Hommes, N. J. R.; Guerra, C. F.; Baerends, E. J. *Organometallics* **1996**, *15*, 2923.

(30) Guerra, C. F.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.

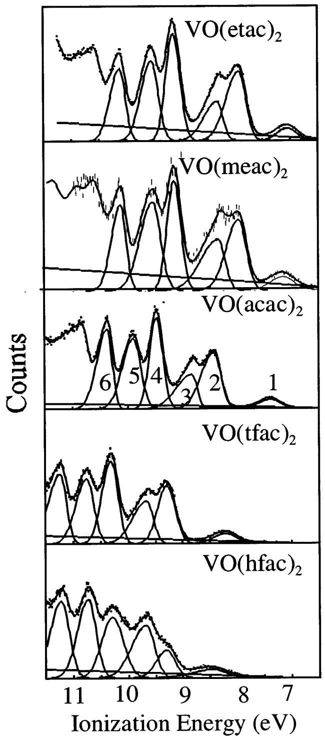

Figure 2. HeI photoelectron spectra of the five complexes.

Table 1. Comparison of the Ionization Energies (eV) for the Five Complexes

peak	VO(etac)$_2$	VO(meac)$_2$	VO(acac)$_2$	VO(tfac)$_2$	VO(hfac)$_2$
1	7.05	7.15	7.36	8.21	8.43
2	7.91	7.94	8.41	9.29	9.30
3	8.25	8.26	8.82	9.66	9.68
4	9.13	9.19	9.47	10.31	10.29
5	9.55	9.59	9.89	10.75	10.73
6	10.13	10.19	10.36	11.23	11.22

Our spectrum of VO(acac)$_2$ is in general agreement with the previous report,[17] though our measured ionization energies differ slightly due to the use of symmetric Gaussians in the previous report, and by the improved resolution and precision of our experiment. The ionization assignments are consistent with reports for the free ligands,[31] and for other metal−acac analogues,[18−20,32,33] and can also be compared to the results from ab initio and density functional molecular orbital calculations (vide infra).

The spectrum of each complex contains features below 11 eV that can be fit with six Gaussian peaks labeled 1−6 in order of increasing ionization energy, with the positions of the Gaussians listed in Table 1. Peak 1 in all spectra is assigned as arising from ionization of the unpaired electron in the predominantly metal $d_{x^2-y^2}$-based orbital (a_1 in C_{2v} symmetry), while peaks 2−5 are assigned as arising from removal of electrons from acac σ and π type orbitals. Peak 6 and additional higher energy portions of the spectra are attributed to ionizations from V−O π and oxo lone pair orbitals of the vanadyl group. Overlapping ionizations makes it difficult to unambiguously assign additional ionizations.

Table 2. Kohn−Sham Eigenvalues and Mulliken Population Analysis of Selected VO(acac)$_2$ Orbitals

		population %				
MO	$-\epsilon$ (eV)	V (orbital)	O (VO)	4O (acac)	2(C$_3$H) (acac)	4CH$_3$ (acac)
16a$_1$ (SOMO)	2.70	89.3 ($d_{x^2-y^2}$)	0	7.8	1.1	0
13b$_2$	5.79	0	4.7	35.6	55.5	0
15a$_1$	6.08	0	4.2	27.9	58.8	0
11b$_1$	6.34	0	10.2	66.0	10.1	8.6
9a$_2$	6.75	8.3 (d_{xy})	0	63.9	14.6	8.5
12b$_2$	7.01	3.0 (p_y)	26.3	51.2	4.7	4.1

Assignment of the majority of lower energy valence ionizations of transition-metal-containing molecules is often possible by comparison of ionization band shapes, by comparison of spectra collected with different photon sources, and by comparison of shifts of the ionizations as different substituents are added. A detailed assignment is difficult for these molecules because all of the ionizations shift together as substituents are added, and the large amount of oxygen character in the majority of the valence orbitals, other than the d^1 ionization, lends little cross-sectional data other than confident assignment of the first ionization. Due to these limitations of empirical evidence, computational results from extensive SCF calculations were previously used to assign the spectrum of VO(acac)$_2$.[17] This current study has revealed nothing that raises serious doubt with these assignments; however, some degree of caution must be used in interpreting any computational results without appropriate experimental support. The conclusions of this study are not dependent upon assignment of the ionizations beyond the general assignments given above.

Computational Results. The assignment of the ordering of ionizations was supported in the previous report by SCF calculations.[17] For further comparison DFT calculations were performed on VO(acac)$_2$ at the GGA (BLYP) level, with Kohn−Sham one-electron orbital energies and Mulliken populations listed in Table 2. We chose this method because one-electron Kohn−Sham orbital energies of ground-state molecules have been proven useful in approximating ionization potentials.[34−39]

The DFT calculations gave an ordering and character of the valence orbitals that are in general agreement with the previous SCF calculations.[17] Two main differences would be expected, and are observed, to exist between the computational results from the two methods. First, the SCF calculation did not place the predominantly $d_{x^2-y^2}$-based orbital as the SOMO, even when ΔSCF calculations were performed, due to the large amount of SCF relaxation energy associated with the very localized V 3d-based orbital. Second, the Kohn−Sham one-electron orbital energies are all much lower than the observed ionization energies due to the poor asymptotic behavior of the Kohn−Sham potentials derived

---

(31) Schweig, A.; Vermeer, H.; Weidner, U. *Chem. Phys. Lett.* **1974**, *26*, 229−233.

(32) DiBella, S.; Fragala, I.; Granozzi, G. *Inorg. Chem.* **1986**, *25*, 3997.

(33) Shcheka, O. L.; Vovna, V. I. *J. Electron Spectrosc. Relat. Phenom.* **1992**, *60*, 211.

(34) Chong, D. P.; Gritsenko, O. V.; Baerends, E. J. *J. Chem. Phys.* **2002**, *116*, 1760.

(35) Stowasser, R.; Hoffman, R. *J. Am. Chem. Soc.* **1999**, *121*, 3414−3420.

(36) Politzer, P.; Abu-Awwad, F. *Theor. Chim. Acta* **1998**, *99*, 83−87.

(37) Politzer, P.; Abu-Awwad, F. Murray, J. *Int. J. Quantum Chem.* **1998**, *69*, 607−613.

(38) Zhao, Q.; Parr, R. G. *J. Chem. Phys.* **1992**, *98*, 543−548.

(39) Zhao, Q.; Parr, R. G. *Phys. Rev. A* **1992**, *46*, 2337−2343.

from the BLYP functional. The difference between the Kohn–Sham SOMO and the observed first ionization energy is 4.66 eV, and in general this difference is about 5 eV for the approximate LDA and GGA functionals typically currently used.[40]

Comparison of Ionization Source Energy Changes. The assignments of the HeI photoelectron spectra of the five complexes suggest that orbitals primarily of vanadium and oxygen character dominate the frontier electronic structures of these complexes. Following the aufbau principle,[41] the lone electron on the vanadium center should lie highest in energy. This is supported by other spectroscopic evidence which also shows that the primarily acac-based orbitals lie next lowest, followed by electrons localized in the V=O interaction.[42,43]

The character of the orbitals from which electrons are removed can be ascertained by changing the ionizing source in the photoelectron experiment. After corrections for instrument resolution and sensitivity, and for other excitation lines in the sources, photoelectron spectra obtained with different photon sources differ only in the intensity of the bands. These intensity changes are related to the character of the orbital from which ionization occurs.[9] From theoretical estimates,[44] the photoionization cross section of V 3d orbitals increases by a factor of 1.6 with respect to O 2p orbitals and 1.4 with respect to C 2p orbitals upon changing photon source from HeI (21.2 eV) to HeII (40.8 eV). Comparison of experimental data to theoretical cross sections has proven useful in the assignment of the photoelectron spectra of transition-metal complexes.[45] The atomic photoionization cross sections indicate that if the ionizations labeled 1 in Figure 1 do indeed arise from orbitals that are predominately vanadium in character, and the remainder of the spectral features arise from orbitals which are predominately oxygen in character, then peaks 1 should grow upon changing ionizing source from HeI to HeII.

As an example, the HeI and HeII spectra of $VO(tfac)_2$ are shown in Figure 3, with information on the relative areas of the Gaussians used to deconvolute the HeI and HeII spectra of $VO(acac)_2$, $VO(etac)_2$, and $VO(tfac)_2$ listed in Table 3. This data clearly illustrates that the intensity of peak 1 increases dramatically with respect to the remainder of the spectrum as the incident photon energies are changed from HeI to HeII, indicating that peak 1 in all cases arises from an orbital which is predominately localized on the vanadium center. Additional smaller intensity changes are observed for the individual ligand ionizations for each of these complexes. These can be attributed to the admixture of metal, oxygen, and carbon character in the orbitals from which these ionizations originate; however, no clear trends are observed and additional evidence for more in-depth assignment of the ionizations is not found.

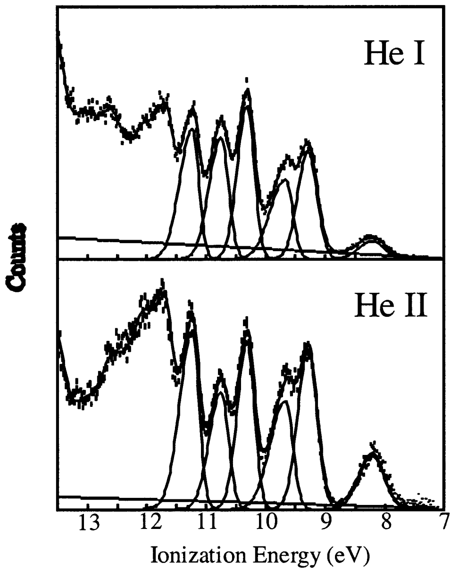

Figure 3. HeI/HeII spectra of $VO(tfac)_2$.

Table 3. Relative Areas of Peaks upon Changing Photon Source[a]

	$VO(acac)_2$		$VO(etac)_2$		$VO(tfac)_2$	
peak	HeI	HeII	HeI	HeII	HeI	HeII
1	0.18	0.33	0.33	0.54	0.22	0.43
2	1.00	1.00	1.00	1.00	1.00	1.00
3	0.65	0.97	1.90	2.00	0.85	0.78
4	1.12	1.24	1.94	1.52	1.28	0.94
5	1.17	1.00	1.97	1.55	1.13	0.73
6	1.10	1.23	1.46	1.62	1.21	1.11

[a] Peak 2 is taken as the reference.

Comparison of Observed Ionization Energy Shifts. The ionization energies observed in the spectra exhibit shifts that are consistent with the qualitative changes in Lewis basicity expected for the ligands. The high electronegativity of the fluorine substituents on the tfac and hfac ligands leads to a removal of electron density from the ligand π system, σ framework, and metal, resulting in stabilization of the ionizations. Therefore, the feature arising from ionization of the metal $d_{x^2-y^2}$ electron (band 1) is stabilized by 0.83 eV upon addition of the three fluoro groups in the tfac ligand, and by 1.1 eV in the case of hfac. The remaining peaks, assigned as primarily oxygen based, show a similar stabilization for $VO(tfac)_2$ and $VO(hfac)_2$. The electron-donating alkyl groups lead to a less dramatic, but still evident, destabilization of the orbitals. For instance, band 1 is destabilized by 0.22 eV for $VO(meac)_2$ and 0.33 eV in the case of $VO(etac)_2$. Interestingly, all of the ionization features for this series of molecules shift by about the same amount as the substituents on the acac ligands are varied. This is in contrast to the behavior that is typically observed; substituents should have the largest effect on ionizations from orbitals localized closest to the substituted site. For example, previous studies of methylated and halogenated cyclopentadienyl complexes have all shown that the predominantly cyclopentadienyl based ionizations are shifted by substitution on the ring to a different extent than the predominantly metal based ionizations.[9–13] The equal shifts of all the ionizations for these molecules indicate that the electronic influences from the

---

(40) Baerends, E. J.; Gritsenko, O. V. *J. Phys. Chem. A* **1997**, *101*, 5383.
(41) Bohr, N. *Philos. Mag.* **1913**, *26*, 476.
(42) Ballhausen C. J.; Gray H. B. *Inorg. Chem.* **1962**, *1*, 111–122.
(43) Casihn, B.; Cunningham, D.; Daly, P.; McArdle, P.; Munroe, M.; Chonchubhair, N. N. *Inorg. Chem.*, **2002**, *41*, 773–782.
(44) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data Tables* **1985**, *32*, 1–14.
(45) Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379.

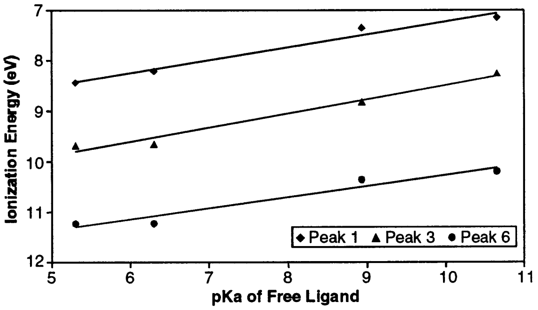

Figure 4. Plot of pK_a as a function of ionization potential.

acac ligand substituents have a noticeable effect upon the electron density. This effect is most likely responsible for the reported differences in structure and reactivity for these complexes.[24]

Relationship of Ionization Energies to Ligand pK_a. The relative donor properties of ligands are often inferred from the pK_a of the free ligands or their neutral conjugate acids. Higher pK_a values should correspond to better donor properties. For these complexes higher pK_a values of the free ligand[46,47] correlate linearly to a destabilization of the orbitals in the metal complexes of hfac, tfac, acac, and meac, consistent with the higher electron density located on the oxygen atoms. Figure 4 illustrates a plot of the pK_a of the neutral conjugate acids of hfac, tfac, acac, and meac (the pK_a of etac has not been reported in the literature) vs ionization energy for the series of molecules. The three ionizations chosen for this figure have been assigned, both here and in the previous report,[17] as metal-based (peak 1), acac ligand-based (peak 3), and VO-based (peak 6). All of the clearly observed ionizations show a linear trend with pK_a (R^2 values of 0.942−0.974). Figure 4 also illustrates that all ionizations are shifted by almost the same amount by the substituents. The slopes of the lines are very similar, ranging from −0.22 eV/pK_a for peak 6 to −0.30 eV/pK_a for peak 2. The linear relationship that is observed for the ligands for which the pK_a is known allows the pK_a of etac to be approximated from the observed trend. Based on the ionization energies of VO(etac)$_2$ the pK_a of etac must only be slightly higher than that of meac.

A linear relationship between ionization energies and pK_a is also seen from the photoelectron data for other homoleptic complexes of acac and its derivatives.[18−21] There is a larger substituent effect upon the ligand-based ionizations of these systems than what is observed for the vanadyl complexes. Table 4 gives ionization energies for selected homoleptic complexes of acac and hfac. Ti(ac)$_3$ [ac = acac or hfac] was chosen because these Ti(III) complexes have the same doublet ground state as the complexes here; the V(III) derivatives were chosen to show that metal center and formal oxidation state have little effect on the shift. To show that this difference cannot be simply attributed to the different number of ac donors and symmetry, we include the *bis* Cu(II) complexes, which also have a doublet ground state, and the Zn(II) analogues, which have a pseudo-tetrahedral (D_{2d}) symmetry. Unlike with the other complexes, the first ionization in the Zn complex is ligand-based; however the first ligand-based ionization (band 2) in the VO complexes shows a similar shift (0.89 eV) to band 1. The smaller ionization shifts for the vanadyl systems indicate that the presence of the oxo ligand is in some part dampening the influence of the acac substituents.

Table 4. Comparison of First Ionization Energies (eV) of Various Metal acac Complexes

	VO(ac)$_2$	Ti(ac)$_3$	V(ac)$_3$	Cu(ac)$_2$	Zn(ac)$_2$
ac = acac	7.36	5.90	6.75	8.20	8.46
ac = hfac	8.21	7.94	8.68	9.92	10.35
Δ	0.85	2.04	1.93	1.72	1.89
ref	this work	18, 20	18	20, 21	21

In conclusion, the experimental results presented here indicate that electronic perturbations at the acac ligand periphery of these complexes have a pronounced effect on the electron density on the acac ligand, at the metal center, and into the oxo ligand of the vanadyl group. Also, there exists a linear correlation between the ionization energies of the VO^{2+} complexes and the pK_a of the conjugate acids of the ligands, indicating that the pK_a's give a good approximation of the relative donor abilities of these ligands.

Acknowledgment. We wish to thank Dr. D. Crans (Colorado State University) for providing initial samples of VO(meac)$_2$ and VO(etac)$_2$ and Drs. D. Lichtenberger (Arizona) and G. Crundwell (CCSU) for helpful discussions. A CSU-AAUP Grant supported this work.

IC0256056

---

(46) Jones, J. R.; Patel, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 574−575.

(47) Bruice, P. Y. *J. Am. Chem. Soc.* **1990**, *112*, 7361−68.