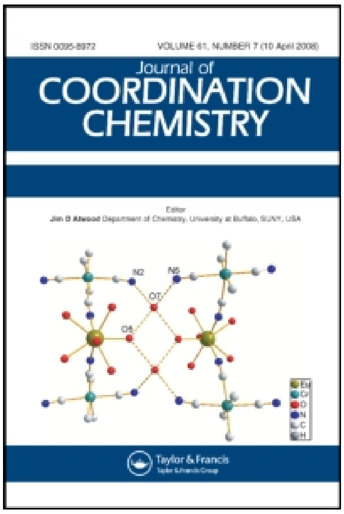

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CORE BINDING ENERGIES OF SOME METAL β-DIKETONATES AND β-DIKETONES IN THE VAPOR PHASE

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To cite this Article Schaaf, Theodore F. , Avanzino, Steven C. , Jolly, William L. and Sievers, Robert E.(1976) 'CORE BINDING ENERGIES OF SOME METAL β-DIKETONATES AND β-DIKETONES IN THE VAPOR PHASE', Journal of Coordination Chemistry, 5: 3, 157 — 161

To link to this Article: DOI: 10.1080/00958977608073003

URL: http://dx.doi.org/10.1080/00958977608073003

J. Coord. Chem.
1976, vol. 5, pp. 157–161

CORE BINDING ENERGIES OF SOME METAL β-DIKETONATES AND β-DIKETONES IN THE VAPOR PHASE

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(Received October 3, 1975)

The vapor-phase core binding energies of some *tris* β-diketonates of Al(III), V(III), Cr(III), and Fe(III) and of two β-diketones have been measured. The rather large shifts observed for the Al 2p energies are believed to be caused mainly by changes in the electrostatic potential at the Al atom due to changes in the charges of the ligand atoms. Considerable resonance relaxation energy is associated with the core ionization of the carbonyl carbon atoms and the CH carbon atoms. The data for the metal hexafluoroacetylacetonates show that the metal d orbitals are not significantly involved in the bonding and suggest that there is no strong ligand→metal donor bonding.

INTRODUCTION

X-ray photoelectron spectroscopy has been shown to be a useful technique for determining atomic charge distributions within molecules, particularly when applied to molecules in the gas phase[1,2]. We have used this technique to obtain the core electron binding energies of a series of volatile *tris* β-diketonate complexes in order to study the valence electron distribution and bonding in these compounds. The β-diketonate ligands studied were hexafluoroacetylacetonate (hfa), trifluoroacetylacetonate (tfa), acetylacetonate (acac), and 2,2,6,6-tetramethyl-3,5-heptanedionate (thd). The compounds and measured core binding energies are listed in Table I. We shall separately discuss three aspects of the data: (1) the trend in the aluminum binding energies, (2) the ligand atom binding energies of the aluminum complexes, and (3) the ligand atom binding energies of all the hfa complexes.

DISCUSSION

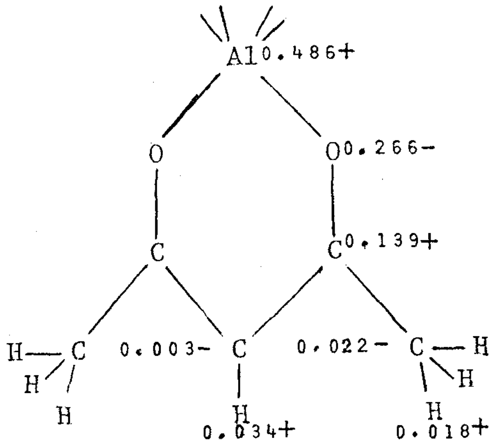
The Aluminum Binding Energies

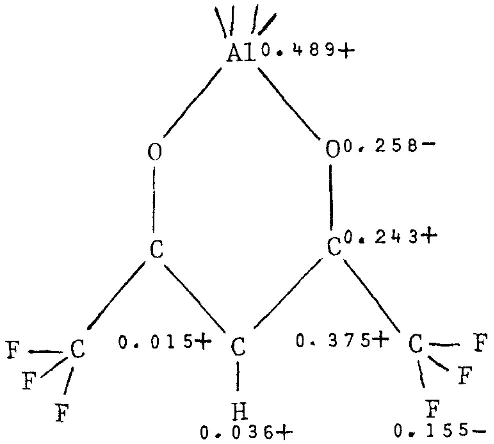
A chemical shift in core binding energy can be equated to the sum of three terms: (1) a term proportional to the change in the charge of the atom that undergoes core ionization, (2) the change in electrostatic potential at the site of the core ionizing atom due to the charges of the other atoms in the two molecules, and (3) the change in the relaxation energy associated with core ionization[1,2].

$$\Delta E_B = k\Delta Q + \Delta V + \Delta E_R \qquad (1)$$

In the case of the *tris* β-diketonates of aluminum, the molecular structure in the vicinity of the aluminum atoms is unchanged, and we believe it is a good approximation to assume that changes in the relaxation energy are zero for the aluminum 2p binding energies. Thus in this case we may write $\Delta E_B \approx k\Delta Q + \Delta V$.

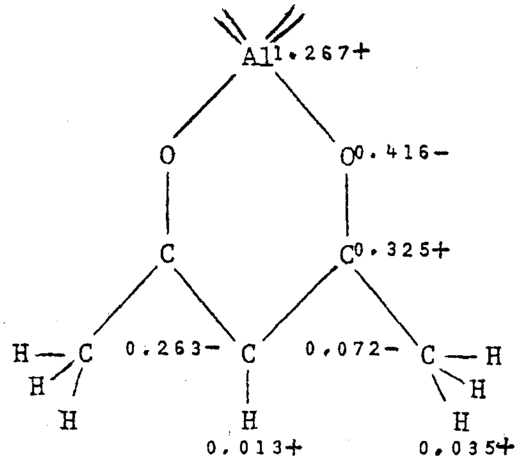
One method for estimating the atomic charges in such complexes is the CHELEQ electronegativity equalization method[2]. We have used this method to calculate the atomic charges in $Al(hfa)_3$ and $Al(acac)_3$ by making the assumptions that the aluminum atom uses only s and p valence orbitals, that the the ligand atoms in the rings use sp^2 hybrid orbitals in their sigma bonds, and that the bond order between the ligand atoms in the rings is 1.5. We found that we could obtain exact agreement between the calculated and observed shift (2.11 eV) by assuming that the CH_3 carbon atoms in $Al(acac)_3$ use sp^3 hybrid orbitals and that the CF_3 carbon atoms in $Al(hfa)_3$ use orbitals with 10% s character in the C–F bonds and orbitals with 70% s character in the C–C bonds. The calculated CHELEQ charges are shown in the following structures.

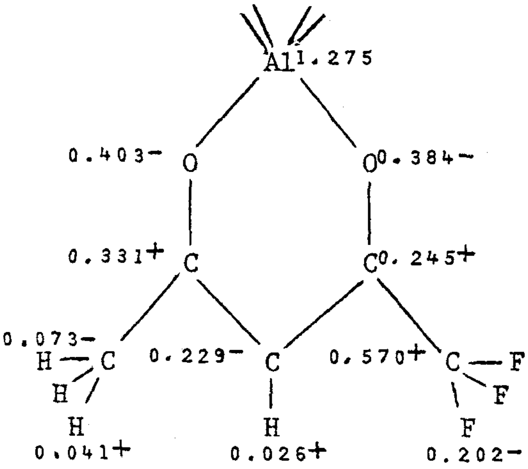




The change in the CHELEQ aluminum atom charge is so small that a reasonable k value of 10.4 corresponds to a negligible value (0.03 eV) for $k\Delta Q$. (The value of 10.4 is estimated from the first ionization potential of aluminum and the second ionization potential of silicon, using the equivalent cores approximation.)

A second method which we have used for estimating atomic charges is the CNDO/2 method[3]. Our CNDO/2 computer program cannot be used to make calculations on molecules having more than 35 atoms or more than 80 valence atomic orbitals; therefore we approximated the desired calculations by calculating the atomic charges for the following bis(formato)-mono(β-diketonato) complexes: $(HCO_2)_2Al(acac)$ and $(HCO_2)_2Al(tfa)$. The calculated CNDO/2 atomic charges in the β-diketonate rings of these hypothetical complexes are shown in the following structures.





By assuming that the atomic charges in $Al(acac)_3$ and $Al(tfa)_3$ are the same as those indicated in the appropriate structures above (but using three times the indicated change in charge for the aluminum atom), and by estimating $k = 10.4$ for aluminum, we calculate

$$\Delta E_B = k\Delta Q + \Delta V = 0.25 + 0.69 = 0.94 \text{ eV}$$

This calculated value is remarkably close to the observed shift, 1.08 eV. In this case the change in the aluminum atom charge is not negligible; nevertheless the ΔV term is almost three times as large as the $k\Delta Q$ term.

It is interesting that these two very different methods can give atomic charges consistent with the observed chemical shifts, even though the calculated charge distributions are very different. According to the CNDO/2 calculations, replacement of a CH_3 group by a CF_3 group causes the carbon atom to which the group is attached to become less positive and the other atoms of the ring to become more positive or less negative. Results of this type have been previously noted in CNDO calculations[4], *ab initio* calculations[5], and XPS-derived charges[6]. On the other hand, the CHELEQ atomic charges show the classical inductive effect upon replacement of a CH_3 group by a CF_3 group. Probably the only clear-cut lesson to be learned from the aluminum binding energy data is that, even if large chemical shifts in the binding energy of a metal are observed on going from one compound to another, the change in the metal atom charge may be very small.

It has been well documented that core electron binding energy shifts can be closely correlated with chemical reaction energies[7,8]. One might expect a good correlation between the aluminum binding energies in these chelates and the aqueous pK values of the corresponding β-diketones[9-12]. A plot of these quantities against one another is shown in Figure 1. The point for thd lies off the straight line because of what we believe is an abnormally high aqueous pK value for H(thd). This diketone has two bulky t-butyl groups which may hinder hydration of the anion. Presumably a correlation of the binding energies with gas-phase pK values would not show this anomaly.

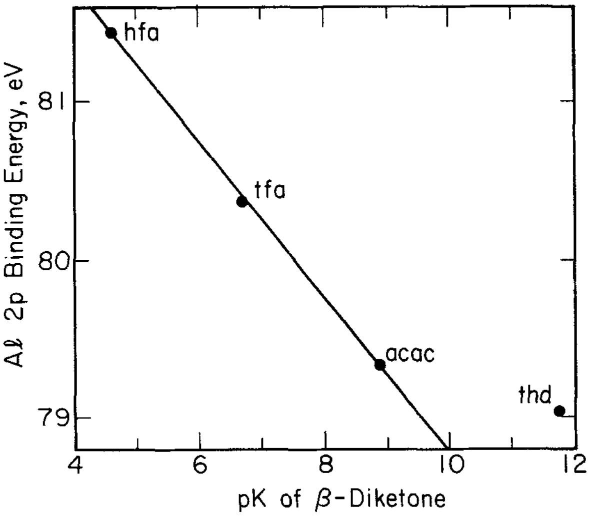
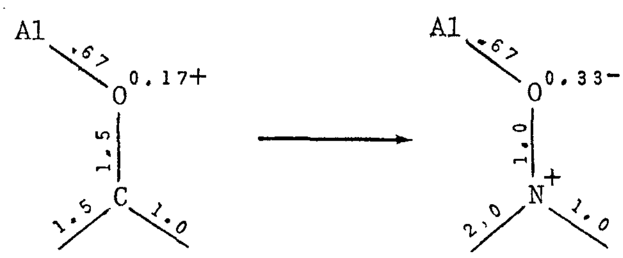


FIGURE. 1 A plot of Al 2p binding energies of *tris* β-diketonates vs aqueous pK values of the corresponding β-diketones. Data from Table I and Refs. 9-12.

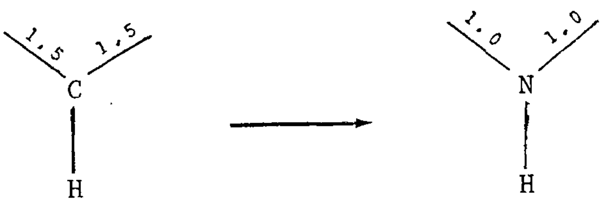
The Ligand Atoms of the Aluminum Complexes

Among the aluminum complexes, the binding energies of a ligand atom of a particular type qualitatively follow the same trend as the binding energies of the aluminum atom, i.e., $Al(hfa)_3 > Al(tfa)_3 > Al(acac)_3 > Al(thd)_3$. This trend is that expected when one stepwise replaces the fluorine atoms of the CF_3 groups with the more electropositive hydrogen atoms and then with the more polarizable CH_3 groups. The decrease in binding energy is undoubtedly due to a reduction of both the absolute atomic charge and the electostatic potential term and, in some cases, to increased relaxation (more negative E_R).

We have used the CHELEQ method (assuming the bonding in the chelate rings to be as we have described above), and equation 1 (using k and l values empirically evaluated from data for compounds with unambiguous structures[13]) to calculate the absolute values of the ligand atom binding energies for the aluminum complexes. We obtained fairly good agreement for the fluorine atoms (deviation ∿ 0.14 eV), the oxygen atoms (deviations < 0.5 eV), and the CX_3 carbon atoms (deviations ⩽ 1.08 eV), but the calculated values for the carbonyl and CH carbon atoms were much too high (by as much as 3.0 eV in the case of $Al(hfa)_3$). We believe the latter discrepancies were due to unaccounted-for relaxation in the core-ionized molecules. In the case of the core ionization of the carbonyl carbon atom (in which the core is effectively converted to that of a nitrogen atom), the resonance structure weighting probably changes in the direction indicated:



This relaxation process corresponds to a shift of negative formal charge to the oxygen atom bonded to the core-ionized carbon atom. In the case of the CH carbon atom, the resonance structure weighting probably changes in the following direction:



The latter relaxation process corresponds to putting lone pair electron density on the core-ionized atom.

The Ligand Atoms of the hfa Complexes

The binding energies of the carbon, oxygen, and fluorine atoms in the several hfa complexes change very little on going from one metal complex to another. Thus there is no evidence for participation of metal d orbitals in the bonding of the transition metal complexes. The same conclusion has been reached by other investigators with respect to acetylacetonate complexes on the basis of structural[15], magnetic[15,16], and spectroscopic[15,17] data. The carbon 1s binding energies of the hfa complexes are not much shifted from those of H(hfa), which exists entirely in the enol form[14]. However the fact that the H(hfa) oxygen 1s binding energies are greater than that of the metal hfa complexes suggests that there is no strong ligand→metal donor bonding in the hfa complexes.

EXPERIMENTAL

Spectra were obtained using the Berkeley iron-free double-focusing magnetic spectrometer[18] The β-diketones and the metal hexafluoroacetylacetonates were placed in a glass vessel connected to the irradiation chamber by a short length of stainless steel tubing. The other metal complexes were placed in a copper chamber which was heated just enough to provide sufficient vapor pressure (*ca* 2×10^{-2} torr) to obtain a good spectrum. Magnesium Kα X-rays (1253.6 eV) were used. Either neon or argon was introduced with the samples, and the Ne 1s line (E_B = 870.23 eV) and the Ar $2p_{3/2}$ line (E_B = 248.45 eV) were used as references. Binding energies were determined by a least-squares fitting of the data to Lorentzian line shapes. The relative accuracies of the peak positions are generally about ± 0.05 eV, however the data in Table I given to only one decimal place are believed to be accurate to ± 0.1 eV. The reported binding energies are absolute free-molecule ionization potentials, with absolute uncertainties of ± 0.1 eV, or, in a few cases, ± 0.2 eV.

V(hfa)$_3$ was prepared by a method analogous to that for Al(hfa)$_3$, described by Morris, et al.[19]. Al(hfa)$_3$ was prepared by the reaction of anhydrous aluminum chloride with H(hfa) in CCl$_4$ and was recrystallized from the same solvent. Fe(hfa)$_3$ was prepared by reaction of aqueous iron(II) chloride

TABLE I.
Core Binding Energies of Metal β-Diketonates and β-Diketones

Compound	Binding Energy, eV						
	Metal 2p	O 1s	F 1s	C 1s			
				CF$_3$	CO	CH	CH$_3$
Al(thd)$_3$	79.03	536.46			291.0		289.83[a]
Al(acac)$_3$	79.33	536.70			291.93	289.24	290.31
Al(tfa)$_3$	80.36	537.75	693.72	298.05	293.00	290.30	291.09
Al(hfa)$_3$	81.44	538.77	694.27	298.66	293.89	291.2	
V(hfa)$_3$	522.34[b]	538.64	694.29	298.64	293.74	290.93	
Cr(hfa)$_3$	584.0[b]	538.72	694.33	298.69	293.81	290.99	
Fe(hfa)$_3$	---	538.75	694.37	298.94	294.14	291.33	
H(hfa)		539.01[c] 540.30	694.55	298.90	294.22	291.5	
H(acac)		537.51[d] 538.55			292.80		290.75[a]

[a] Combination peak due to all non-carbonyl carbon atoms.

[b] $2p_{3/2}$ level.

[c] Assuming equal intensities for the two lines, the FWHM values were 1.4 and 1.2 eV for the lower and higher E_B lines, resp.

[d] The line of lower E_B (FWHM = 1.3 eV) was about 0.7 as intense as the other (FWHM = 1.5 eV).

with a hexane solution of H(hfa). The products were purified by sublimation. $Cr(hfa)_3$ was synthesized by the method of Sievers, et al.[20] by heating chromium(III) nitrate nonahydrate and H(hfa) in ethanol. The product was recrystallized from CCl_4. $Al(acac)_3$ was prepared as described by Young[21] and the product was recrystallized from benzene by the addition of hexane. $Al(tfa)_3$ and $Al(thd)_3$ were synthesized by analogous methods except that they were purified by fractional sublimation *in vacuo*. The H(hfa) and H(acac) were purified by fractional distillation immediately before obtaining their spectra.

The CNDO/2 calculations were made using the parameters for hydrogen and the first-row elements given by Pople and Beveridge[3]. For aluminum we used Santry and Segal's[22] method of parameterization, Hinze and Jaffé's[23] orbital ionization energies and electron affinities, and Cusachs and Corrington's[24] valence s orbital wavefunctions. Structural data required in the CNDO/2 and CHELEQ calculations were estimated from the parameters given for $Al(acac)_3$[15]

ACKNOWLEDGEMENTS

We are grateful to Mr. Albert Bakke for assistance in obtaining the spectrum of H(hfa). This work was supported by the National Science Foundation (Grant GP-41661X) and the U.S. Energy Research and Development Administration.

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