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The Electron-Impact Ionization Potentials of Successively Substituted Acetylacetonates of Chromium(III)

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Recent interest[3-5] in the apparently abnormal behavior of the ionization potentials of series of transition metal chelate compounds postulated from the application of Koopmans' theorem[6] to Barnum's Hückel molecular orbital calculations for the compounds[7] prompts us to report data relevant to this problem.

On the basis of substituent-effect studies, it has been suggested[3b] that the electron removed by low-energy electron impact is one from the π system dominated by the ligand, not from a metal-dominated orbital. This conclusion was supported by the magnitude of the substituent effect on ionization potentials of substituted chromium(III) acetylacetonate complexes, which is similar to that found for substituent effects on ionization potentials of substituted benzene rings, as one would expect for the removal of an electron from a ligand π orbital. The poor correlation between the ionization potentials and Hammett σ constants was taken as an indication that the electron is not removed from a metal-dominated orbital. We have reported studies on copper chelates with mixed ligands which indicate that the orbital from which the electron is removed is affected equally by both ligands,[5] and we now report experiments extending this conclusion to the chromium(III) chelates of acetylacetone.

We have examined the ionization potentials of a series of chromium(III) chelates, *viz.*, tris(acetylacetonato)chromium(III) (**1**), bis(acetylacetonato)3-nitroacetylacetonatochromium(III) (**2**), acetylacetonatobis(3-nitroacetylacetonato)chromium(III) (**3**), and tris(3-nitroacetylacetonato)chromium(III) (**4**).[8] Since the ionization potential of an unsubstituted ring should be lower than the ionization potential of a nitro-substituted ring (*cf.* benzene, 9.237 eV;[9] nitrobenzene, 9.92 eV[9]), then the ionization potential should reflect removal of degeneracy of filled molecular orbitals (the HFMO if Koopmans' theorem applies) in the unsymmetrically substituted compounds, if the orbital from which the electron is removed has a strong contribution from the ligand. A simplistic extension of this model would draw a parallel to the observation that the ionization potential of a polysubstituted alkane is the same, within experimental error, as the ionization potential of the structurally analogous monosubstituted alkane having the lowest IP:[10] the ionization potential would remain low for compounds **1**, **2**, and **3**, where ionization would occur in an unsubstituted ring, and then rise sharply for compound **4**, where there is no longer an unsubstituted ring to be ionized. As Figure 1 indicates, this condition is not fulfilled; rather there is a smooth linear increase as the number of nitro groups is increased. Obviously another explanation is required; no sort of more sophisticated argument that predicts any abrupt change can be considered.

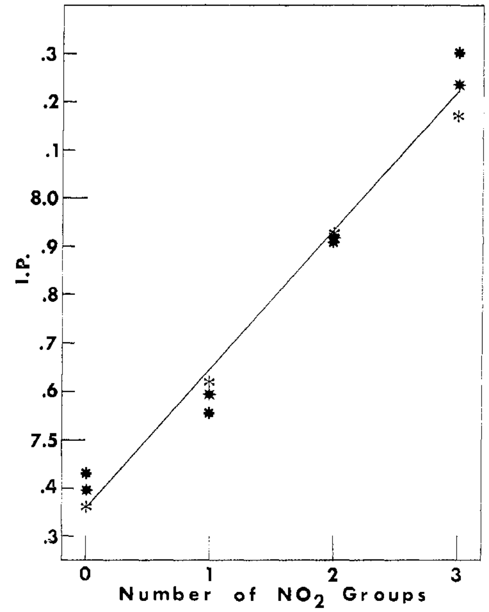

Figure 1.—Linear correlation of ionization potentials of substituted tris(acetylacetonato)chromium(III) chelates with the number of nitro groups substituted at the 3 positions. Pinwheels and asterisks refer to averages of data obtained with two different ion sources; the eight-point stars are their averages, through which a least-squares line was drawn.

A possible explanation is that the electron is removed from an orbital equally affected by all three ligands. Such an orbital would encompass the metal atom, and would probably contain a large amount of metal character. This explanation seems to contradict the mounting body of evidence[3,4] against the removal of an electron from a metal-dominated orbital, but these arguments rely on the accuracy of Barnum's calculations, which have recently come under question.[11]

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(3) (a) G. M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, **7**, 870 (1968); (b) G. M. Bancroft, C. Reichert, J. B. Westmore, and H. D. Gesser, *ibid.*, **8**, 474 (1969); (c) C. Reichert and J. B. Westmore, *ibid.*, **8**, 1012 (1969).

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(8) W. L. Young, III, Ph.D. Dissertation, University of North Carolina, 1964. We are indebted to Professor James P. Collman for a generous gift of these compounds.

(9) "Ionization Potentials, Appearance Potentials, and Heats for Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C. 1969. The quoted values are an average of "best" spectroscopic and photoionization values and the photoionization value, respectively.

(10) H. J. Svec and G. A. Junk, *J. Amer. Chem. Soc.*, **89**, 790 (1967).

(11) E. A. Magnusson, K. A. Thomson, and A. G. Wedd, *Chem. Commun.*, 842 (1969).

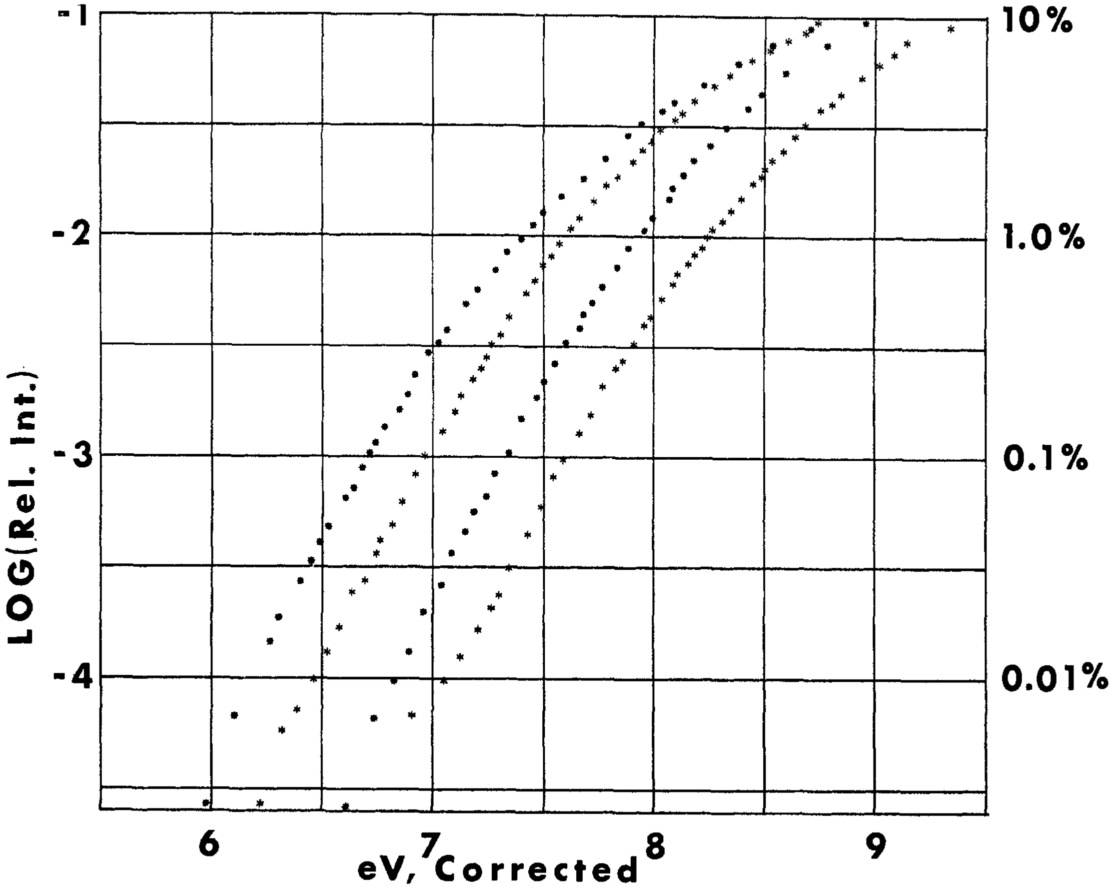

Figure 2.—Ionization efficiency curves representative of data from which data represented by asterisks in Figure 1 were taken; the curves, left to right, are for compounds **1**, **2**, **3**, and **4**.

Thus we do not reject this model, for it contradicts only arguments based on a much too approximate theory.

Another model[12] would have ionization occur from a large orbital encompassing the whole molecule. This MO would have to be of very low energy.

Again, removal of an electron from a molecule by electron impact is a fast process. It may be then that the electron is removed from the first chelate ring with which the impacting electron interacts. In this fashion our ionization efficiency curves could be considered as the weighed sum of three independent ionization efficiency curves, one from each chelate ring in the system. Thus the curves for the mono- and dinitro compounds result from summing, for the mononitro case, one part of the ionization efficiency curve from the nitro-substituted ring and two parts of the curve of the unsubstituted ring. For the disubstituted case, two parts of the curve for the nitro-substituted ring and one part from the unsubstituted ring are added. This treatment would also result in the linear progression of ionization potentials, as found. It requires that ionization from an unsubstituted ring after energy transfer to a nitro-substituted ring is not important. This should produce breaks in the ionization efficiency curves for the monosubstituted and disubstituted compounds, but, as Figure 2 shows, if these breaks are present, they are masked by the convolution with the energy spread of electrons from the filament. The hypothesis is weakened by the necessary assumption of the inefficiency of autoionization, and in addition a large change in the slope of the ionization efficiency curve of the dinitro compound at the onset of ionization from the two substituted rings should have been detected in spite of the electron energy spread.

Experimental Section

Our data were obtained by a small modification of a statistical method previously described,[13] based on the energy compensation technique of Kiser and Gallegos,[14] which seems applicable to the ionization efficiency curves obtained (*cf.* Figure 2). The small change is to determine the correlation line between experimental meter readings and actual electron voltages (assigned from "best" literature values for the IP's of standards) by a least-squares routine. We bracket the IP of the compound in question with two secondary standard IP's, those of benzene and anthracene, referred to the IP of Xe as a primary standard.[15] Interpolation between standard values <2 V apart was chosen over extrapolation from a point 4 V higher, and though our values depend on the values taken for the IP's of secondary standards, they can be corrected against improved values in the future more easily than

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[12] C. Reichert and J. B. Westmore, Abstracts, 21st Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 5–8, 1969, No. S-38.

[13] C. G. Pitt, M. S. Habercom, M. M. Bursey, and P. F. Rogerson, *J. Organometal. Chem.* (Amsterdam), **15**, 359 (1968).

[14] R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.*, **66**, 947 (1962).

[15] Benzene, 9.237 eV; Xe, 12.13 eV;[9] anthracene, 7.41 eV; the last is the average of two charge-transfer values, 7.40[16] and 7.42 eV.[17]

[16] M. Kinoshita, *Bull. Chem. Soc. Jap.*, **35**, 1609 (1962).

[17] H. Kuroda, *Nature*, **201**, 1214 (1964).

a value extrapolated over a very large distance. The choice of aromatic hydrocarbons as standards was suggested by the consideration that Franck–Condon factors in aromatic hydrocarbons would approximate those in the metal acetylacetonates better than those in smaller molecules would, and of course those in noble gases! These points may account for the discrepancy between our values and the values reported earlier[3b] for compounds **1** and **4**.[18-21]

Data were obtained on a modified Hitachi RMU-6E mass spectrometer in at least sextuplicate on at least two different days for each of the sets of experimental data summarized in Figure 1. The sets of data were repeated with different ion sources. They were recorded at the same accelerating voltage; the closest standard, anthracene, has mol wt 178, and therefore mass discrimination effects should be less than in other studies. Internal correlations for this set and others[5,19] suggest that the data within themselves are good to about ±0.03 eV, as measured by the closeness of fit of data points to correlation lines. While our precision is ±0.02 eV in general, and our internal accuracy for the set 0.03 eV, we of course do not claim absolute accuracy greater than what is generally found for electron-impact methods, ±(0.1–0.2) eV.

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[18] The energy compensation technique gave a high value for the IP of benzene in the original investigation on a time-of-flight instrument.[14] On the other hand, our single-point results were reproduced in another study[19] to within ±0.05 eV on the average by a semilogarithmic-plot[20] method on an MS902 mass spectrometer in which different standards were used.[21]

[19] C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *J. Amer. Chem. Soc.*, **92**, 519 (1970).

[20] F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

[21] D. Rosenthal, personal communication.

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Nuclear Quadrupole Coupling in Bis(tetracarbonylcobalt)tin Compounds

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Prior studies of a series of compounds formed by insertion of a metal-containing group into a $Co_2(CO)_8$ molecule have revealed several features regarding the stretching frequencies and the intensities of the infrared spectra of these compounds.[3] These features include (1) the observation that there is appreciable coupling between the $Co(CO)_4$ groups, (2) a shift to higher frequencies of the CO stretching frequencies with increasing halogen substitution on the metal atom, and (3) an increase in the Co–M–Co bond angle as determined by relative intensity measurements of the infrared bands. The ^{59}Co and ^{35}Cl pure quadrupole resonances have been observed and measured in dichlorobis(tetracarbonylcobalt)tin(IV), $Cl_2Sn[Co(CO)_4]_2$, chlorophenylbis(tetracarbonylcobalt)tin(IV), $Cl(C_6H_5)Sn[Co(CO)_4]_2$, and diphenylbis(tetracarbonylcobalt)tin(IV), $(C_6H_5)_2Sn[Co(CO)_4]_2$. This study of these compounds was made in order to correlate the ir and nqr data and to provide a basis for the establishment of a model of the bonding in the system.

Experimental Section

The compounds studied were prepared by the procedure of Patmore and Graham.[3] Their identity was ascertained by colors, melting points, and infrared spectra. Observations and measurements of the frequencies of the resonances were made using a noise-controlled superregenerative spectrometer.[4] Three-gram samples were used. All measurements were made at 25°. Frequency measurements were made by switching the oscillator to continuous wave operation *via* application of a high voltage to the control grid and measurement of the oscillator frequency with a Hewlett Packard 5245L frequency counter. For known resonances this method gives agreement to ±0.002 MHz.

Results and Discussion

The observed resonances are given in Table I. Also given are the nuclear quadrupole coupling constants, e^2Qq_{zz}, and the asymmetry parameters. For ^{59}Co, which has a nuclear spin $I = {}^7/_2$, both e^2Qq_{zz} and η were obtained from the experimental frequencies by use of series approximations for the transition frequencies.[5] The values were further confirmed by use of a frequency ratio plot.[6]

The occurrence of two resonances for each compound indicates two inequivalent crystallographic sites for the Co atoms in each. If the Co atom is in a trigonal-bipyramidal configuration, then the threefold axis dictates that $\eta = 0$. The values of η observed experimentally are small and are undoubtedly due to intermolecular forces in the crystal and/or nonsymmetrical sites due to crystal packing eliminating the strict C_{3v} site symmetry. This view is substantiated by the fact that there are differences in η for the two crystalline sites in these compounds and that these differences are of the same order of magnitude as the values of η. Were the magnitudes of the η's dependent primarily on the intramolecular bonding, then η should be nearly the same for all sites with the differences being due to intermolecular effects.

To discuss the bonding in this compound one can proceed *via* two paths: (1) comparison of the experimental parameters with those of similar compounds; (2) comparison of experimental coupling constants with calculated coupling constants, based on some molecular model.

The e^2Qq_{zz}'s and η's for the compounds studied along with those of several related compounds are given in Table II. A comparison of the data given in this table leads to several observations. (1) The inductive effect of a Cl atom bonded to a Sn atom will increase the electron affinity of the empty 4d orbitals of the Sn

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[3] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

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