# On the Question of Ring Currents in Metal Acetylacetonates. Electric Field Effects on the Proton Resonances of Cationic and Anionic β-Diketonate Complexes[1]

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Abstract: Proton chemical shifts have been measured in $CDCl_3$ solution for a series of cationic acetylacetonato complexes of the types $[M(acac)_3]X$ and $[B(acac)_2]X$ (M = Si, Ge, and Ti; X^- = Cl^-, Br^-, HCl_2^-, ClO_4^-, I_3^-, $AuCl_4^-$, or $SbCl_6^-$) and for the anionic benzoylacetonato and trifluoroacetylacetonato complexes, $[C_5H_{12}N][M-(bzac)_4]$ and $[C_5H_{12}N][M(tfac)_4]$ (M = La and Y). Some of these compounds have not been reported previously. The methyl and ring proton (-CH=) resonances of the cationic complexes are shifted downfield relative to the resonances of analogous, neutral metal diketonates, whereas the resonances of the anionic complexes are shifted upfield. The observed shifts are examined in relation to the charge on the ion and the hypothesis of benzenoid ring currents. Point charge model calculations indicate that the shifts can be satisfactorily accounted for in terms of the electric field caused by the charge on the ion, and there is no need to invoke ring currents. The -CH= resonances of the cationic complexes depend on the size of the anion and the solution concentration; these dependences are discussed in terms of ion pairing.

The electronic structure of metal acetylacetonates continues to be a subject of great interest and considerable controversy. The results of numerous X-ray diffraction studies[3] indicate that the acetylacetonate portion of the chelate ring is planar and that the two M–O, C–O, and C–C bond distances are equal, thus implying enolate resonance in the chelate ring. This resonance which is indicated explicitly in I is often written as shown in II.
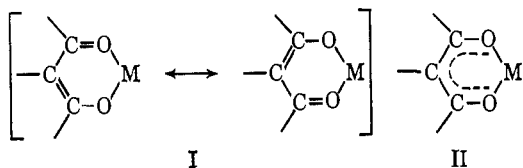
In a study of the formation constants of metal chelates, Calvin and Wilson[4] suggested that the benzenoid resonance structures III, commonly written as IV, may
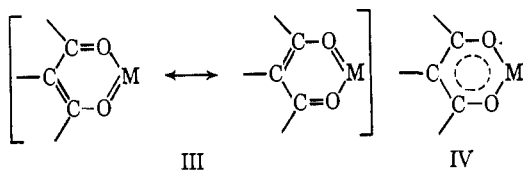
also be important contributors to the electronic structure of metal β-ketoenolates. Although the six-membered chelate ring deviates somewhat from planarity in most acetylacetonate complexes[3b] (there is a fold about the line connecting the two oxygen atoms), the deviations do not appear to be large enough to preclude the possibility of some benzenoid resonance.

Collman[5] has shown that metal acetylacetonates ex-

hibit aromatic chemical behavior in that the chelate rings undergo a wide variety of electrophilic substitution reactions characteristic of aromatic systems. However, attempts to obtain physical evidence for aromaticity have been distinctly less successful; in particular, nmr investigations of the chemical shift of acetylacetonate protons have not afforded convincing evidence for ring currents, which might be expected on the basis of benzenoid structure IV.

Collman[6] and Hester[7] have presented evidence in support of ring currents. Collman, Marshall, and Young[6] noted that substituted tris(acetylacetonate) complexes of the type $M(Xacac)(Yacac)_2$, where the substituents $X \neq Y$ = H, Cl, NO_2, CHO, etc. are located at the γ-carbon atom, gave three methyl resonances of equal intensity. It was pointed out that one of the methyl groups of a Y-substituted ring lies above an X-substituted ring, whereas the other lies above a Y-substituted ring. The chemical shift between the two methyl groups of the Y-substituted rings was attributed to a long-range magnetic anisotropy owing to a difference between the ring currents in the X- and Y-substituted rings. However, the shifts are small (generally 1–2 cps at 60 Mc), and the observed nonequivalence is required by symmetry alone,[8] regardless of whether it is caused by an inductive or electric field effect, a ring current, or some other effect. Shifts of the same magnitude have been observed for the nonequivalent methyl groups of *trans* metal benzoylacetonates[9] and trifluoroacetylacetonates,[10] compounds which contain three identical, unsymmetrical, bidentate ligands. In these compounds, the three chelate rings would presumably have the same ring current, and therefore the nonequivalence appears to have some other origin.

Hester[7] has reported low-field shifts for the methyl

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(2) National Research Council of Canada Predoctoral Fellow, 1966–1968.
(3) References are given in recent reviews by (a) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, 88, 2951 (1966); (b) E. C. Lingafelter, *Coord. Chem. Rev.*, 1, 151 (1966).
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and ring proton (–CH=) resonances of [Si(acac)₃]-[HCl₂]; the –CH= resonance was shifted by −0.86 ppm relative to the enol form of free acetylacetone. These shifts were presented as evidence for "considerable benzenoid resonance" in the chelate ring.

On the other hand, Holm and Cotton[11] had earlier examined the –CH= resonances of ten neutral metal acetylacetonates in carbon tetrachloride solution and found no support for the postulate of benzenoid resonance. The chemical shifts were close to those observed for olefinic protons, and they were nearly independent of the size, charge, and π-bonding ability of the metal ion. Similar conclusions were reached by Smith and Thwaites[12] who pointed out that the –CH= resonances of most acetylacetonate complexes are actually shifted slightly upfield relative to the enol form of free acetylacetone. Therefore, any ring current effect must be masked by an even larger effect which displaces the resonances to higher field.

The principal difference between Si(acac)₃⁺ and the other acetylacetonate complexes thus far examined is the charge on the silicon complex. It is well known that the proton resonances of aromatic carbonium ions[13,14] and alkylcarbonium ions[15] are shifted markedly to low fields. Similar low-field shifts have been observed for the positively charged N(C₂H₅)₄⁺ and As(C₂H₅)₄⁺ ions.[16] Therefore, as has been suggested by Fackler[17] and by Smith and Wilkins,[18] the low-field shifts for Si(acac)₃⁺ can probably be explained in terms of the charge on the ion without the necessity of invoking ring currents in the chelate ring.

In order to explore this possibility, we have investigated the nmr spectra of several cationic acetylacetonate complexes including the boron complex, B(acac)₂⁺, where no ring currents are expected to occur. Some anionic diketonate complexes were also studied with the anticipation that these would exhibit upfield shifts. The observed shifts were then compared with shifts calculated on the basis of the electric field due to the charge on the ion.

Experimental Section

Reagents and Techniques. 2,4-Pentanedione (Matheson Coleman and Bell, bp 136–140°), 1-phenyl-1,3-butanedione (Eastman Organic Chemicals), and 1,1,1-trifluoro-2,4-pentanedione (Columbia Organic Chemicals Co., Inc.) were used as purchased without further purification. Silicon(IV) bromide and germanium(IV) chloride were prepared from the elements by standard procedures.[19] Other metal chlorides were purchased and were reagent grade.

All solvents were reagent grade. Dichloromethane, chloroform, benzene, and ether were dried by refluxing over calcium hydride. Deuteriochloroform was prepared by the method of Paulsen and Cooke.[20]

All complexes containing boron, silicon, germanium, and titanium were prepared and handled under anhydrous conditions in a

dry nitrogen atmosphere. Glassware was dried at *ca.* 140° and was allowed to cool under nitrogen. Melting points were measured with a Thomas–Hoover melting point apparatus using a calibrated thermometer; capillary tubes were plugged with modeling clay to protect samples from the atmosphere. Reported melting points are corrected.

Bis(2,4-pentanedionato)boron(III) Hydrogen Dichloride. This yellow-white compound was prepared as described by Dilthey.[21] Analytical data and an nmr line at *ca.* −11.35 ppm (concentration, 10 g/100 ml of CDCl₃) indicate that the product is [B(acac)₂][HCl₂] rather than B(acac)₂Cl. It is very unstable in air, decomposes on standing *in vacuo* at room temperature, and is best stored under nitrogen in a refrigerator; mp 88–91° dec.

Anal. Calcd for B(C₅H₇O₂)₂HCl₂: C, 42.75; H, 5.38; Cl, 25.24. Found: C, 42.95; H, 5.49; Cl, 24.79.

Bis(2,4-pentanedionato)boron(III) Tetrachloroaurate(III). This compound was prepared by Dilthey's procedure[21] in 44% yield; mp 145–147° dec, lit.[21] 135°.

Anal. Calcd for B(C₅H₇O₂)₂AuCl₄: C, 21.93; H, 2.58; Au, 35.96; Cl, 25.89. Found: C, 22.09; H, 2.65; Au, 36.26; Cl, 25.71.

Bis(2,4-pentanedionato)boron(III) Hexachloroantimonate(V). Freshly prepared B(acac)₂HCl₂ (0.90 g, 3.2 mmoles) was dissolved in *ca.* 25 ml of dry chloroform, and to the resulting red solution was added 0.50 ml of antimony(V) chloride (1.17 g, 3.9 mmoles). Twenty milliliters of dry ether was then added slowly with periodic swirling, which resulted in the formation of an oily product. The mixture was allowed to stand for about 2 hr at 0° with occasional vigorous swirling, whereupon the desired compound crystallized as long, cream-colored needles. These were filtered under nitrogen, washed with two 20-ml portions of anhydrous ether, and dried *in vacuo.* The yield was 1.30 g (75% theoretical); mp 155–157° dec.

Anal. Calcd for B(C₅H₇O₂)₂SbCl₆: C, 22.10; H, 2.60; B, 1.99; Sb, 22.40; Cl, 39.14. Found: C, 22.00; H, 2.57; B, 2.02; Sb, 22.41; Cl, 39.25.

Tris(2,4-pentanedionato)silicon(IV) Hydrogen Dichloride. This compound was synthesized by the method of Riley, *et al.,*[22] mp 172.5–174.5° dec; lit. 171–174° dec,[22] 85–89°,[23] 85–87°.[24] Tris-(2,4-pentanedionato)silicon(IV) chloride was obtained by heating [Si(acac)₃][HCl₂] for 5 hr at 80° *in vacuo;* loss of hydrogen chloride was verified by the nmr spectrum.

Tris(2,4-pentanedionato)silicon(IV) Bromide. 2,4-Pentanedione (19.0 ml, 185 mmoles) dissolved in *ca.* 30 ml of dry benzene was added dropwise with stirring to a solution of silicon(IV) bromide (6.10 ml, 49.5 mmoles) in 100 ml of dry benzene. The addition was followed by brisk evolution of hydrogen bromide and by the appearance of a yellow oily layer. The mixture was refluxed for 1 hr and then allowed to cool to room temperature. The resulting white solid was filtered under nitrogen, washed with 30 ml of dry benzene and two 30-ml portions of anhydrous ether, and dried *in vacuo* for 0.5 hr. The yield was 16.4 g (82% theoretical). Further purification may be effected by recrystallization from dichloromethane–hexane. The compound begins to decompose at ∼200° but does not melt below 300°.

Anal. Calcd for Si(C₅H₇O₂)₃Br: C, 44.45; H, 5.22; Si, 6.93; Br, 19.71. Found: C, 44.27; H, 5.31; Si, 7.15; Br, 20.03.

Tris(2,4-pentanedionato)silicon(IV) Hexachloroantimonate. Antimony(V) chloride (1.20 ml, 9.4 mmoles) dissolved in 25 ml of glacial acetic acid was added dropwise with stirring to a 150-ml glacial acetic acid solution of [Si(acac)₃][HCl₂] (3.10 g, 7.81 mmoles). The reaction mixture was stirred for 1 hr at room temperature, and the resulting white-cream solid was filtered and dried *in vacuo* for 1 day. The yield was 4.15 g (81% theoretical); mp 196–197° dec, lit.[24] 170–172°.

Anal. Calcd for Si(C₅H₇O₂)₃SbCl₆: C, 27.30; H, 3.21; Si, 4.26; Sb, 18.45; Cl, 32.24. Found: C, 27.14; H, 3.16; Si, 4.50; Sb, 18.18; Cl, 32.09.

Tris(2,4-pentanedionato)germanium(IV) Hexachloroantimonate-(V). This compound was prepared in dichloromethane solution in 34% yield by a slight modification of the method of Cox, *et al.;*[24] mp 165–167° dec, lit.[24] 161–163°.

Tris(2,4-pentanedionato)titanium(IV) Perchlorate. Freshly prepared hydrous titanium(IV) oxide (1.5 g) was dissolved with heating

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Table I. Chemical Shifts for Cationic and Anionic Metal Diketonates in CDCl₃ Solution[a]

Compound	Concn, 10.0 g/100 ml		Concn, 4.0 g/100 ml		Concn, 1.0 g/100 ml	
	–CH=	–CH₃	–CH=	–CH₃	–CH=	–CH₃
[B(acac)₂][HCl₂][b]	−6.84	−2.56	−6.80	−2.56	−6.71	−2.54
[B(acac)₂][AuCl₄]	−6.58	−2.55	−6.55	−2.55	−6.51	−2.54
[B(acac)₂][SbCl₆]	−6.56	−2.55	−6.54	−2.55	−6.51	−2.54
[Si(acac)₃]Cl	−6.28	−2.30	−6.25	−2.29	−6.24	−2.29
[Si(acac)₃]Br	−6.31	−2.30	−6.29	−2.29	−6.26	−2.30
[Si(acac)₃][HCl₂][c]	−6.24	−2.29	−6.21	−2.29	−6.20	−2.29
[Si(acac)₃][SbCl₆]	−6.11	−2.28	−6.10	−2.28	−6.08	−2.28
[Ge(acac)₃][SbCl₆]	−6.05	−2.31	−6.03	−2.30	−6.01	−2.30
[Ti(acac)₃][ClO₄]	−6.35	−2.29	−6.33	−2.28	−6.28	−2.27
[Ti(acac)₃]I₃	−6.32	−2.32	−6.30	−2.33	−6.28	−2.33
[Ti(acac)₃][SbCl₆]	−6.26	−2.30	−6.25	−2.30	−6.22	−2.29
[C₅H₁₂N][Y(bzac)₄]	−6.02	−2.07	...	...	...	...
[C₅H₁₂N][La(bzac)₄]	−5.91	−2.02	...	...	...	...
[C₆H₁₂N][Y(tfac)₄]	−5.63	−2.04	...	...	...	...
[C₅H₁₂N][La(tfac)₄]	−5.64	−2.05	...	...	...	...

[a] Ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume); temperature ∼37°. [b] The HCl₂⁻ proton gives a resonance line at ca. −11.35 ppm (10.0 g/100 ml). [c] The HCl₂⁻ proton gives a resonance line at −11.93 ppm (10.0 g/100 ml) and −7.38 ppm (4.0 g/100 ml).

in 25 ml of 9 M sulfuric acid, and the resulting solution was carefully added to 440 ml of 1 M perchloric acid. The titanium(IV) solution was then extracted with a 5 M solution of 2,4-pentanedione in chloroform, and the desired complex was isolated from the organic phase as described by Reynolds;[25] mp 184–185° dec; lit.[25] 183°.

Tris(2,4-pentanedionato)titanium(IV) Triiodide. This compound was prepared by reaction of 2,4-pentanedione with titanium(IV) iodide in ether solution in the presence of molecular oxygen; mp 129–131° dec.[26]

Anal. Calcd for Ti(C₅H₇O₂)₃I₃: C, 24.82; H, 2.92; Ti, 6.60; I, 52.44. Found: C, 24.90; H, 2.93; Ti, 6.48; I, 52.68.

Tris(2,4-pentanedionato)titanium(IV) Hexachloroantimonate. This compound was prepared by reaction of dichlorobis(2,4-pentanedionato)titanium(IV)[27] with antimony(V) chloride in glacial acetic acid using a procedure similar to that described above for the silicon analog; mp 167.5–169.5°; lit.[24] 153–155°.

Anal. Calcd for Ti(C₅H₇O₂)₃SbCl₆: C, 26.51; H, 3.11; Cl, 31.30. Found: C, 26.42; H, 2.99; Cl, 31.50.

Piperidinium Tetrakis(1-phenyl-1,3-butanedionato)yttrate(III).[28] To a boiling mixture of 70 ml of 95% ethanol, 3.16 ml of piperidine (32.0 mmoles), and 5.19 g of 1-phenyl-1,3-butanedione (32.0 mmoles) was added a solution of yttrium(III) chloride (1.56 g, 8.0 mmoles) in 35 ml of water. The reaction mixture was refluxed for 1 hr and filtered by suction, and the filtrate was concentrated by evaporation of solvent until the first sign of turbidity (about one-half the original volume). The solution was then allowed to stand at ∼3° for 1 day, and the resulting pale yellow crystals were collected and dried *in vacuo* for 2 days. The yield was 3.95 g (60% theoretical); mp 120–122°.

Anal. Calcd for C₅H₁₂NY(C₁₀H₉O₂)₄: C, 65.93; H, 5.90; N, 1.71; Y, 10.84. Found: C, 65.93; H, 6.05; N, 1.89; Y, 10.70.

Piperidinium Tetrakis(1-phenyl-1,3-butanedionato)lanthanate(III). This compound was prepared by the procedure used for the yttrium analog. The product consisted of white crystals plus a sticky, yellow solid. The crystals were separated mechanically and dried *in vacuo*: yield 29% theoretical; mp 118–120°.

Anal. Calcd for C₅H₁₂NLa(C₁₀H₉O₂)₄: C, 62.14; H, 5.56; N, 1.61; La, 15.97. Found: C, 62.41; H, 5.75; N, 1.54; La, 16.20.

Piperidinium Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)yttrate(III). This compound was prepared by the same procedure as that used for the corresponding benzoylacetonate. The yield after recrystallization from dichloromethane–hexane was 33% theoretical; mp 106–108°.

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(28) The approach employed here is similar to those used for preparation of analogous europium(III) complexes: (a) L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964); (b) H. Bauer, J. Blanc, and D. L. Ross, *ibid.*, **86**, 5125 (1964).

Anal. Calcd for C₅H₁₂NY(C₅H₄F₃O₂)₄: C, 38.13; H, 3.58; N, 1.78; F, 28.97; Y, 11.29. Found: C, 38.29; H, 3.69; N, 2.01; F, 28.83; Y, 11.50.

Piperidinium Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)lanthanate(III). This compound was synthesized by the method employed for the yttrium analog. The yield after recrystallization from dichloromethane–hexane was 52% theoretical; mp 122–124°.

Anal. Calcd for C₅H₁₂NLa(C₅H₄F₃O₂)₄: C, 35.85; H, 3.37; N, 1.67; F, 27.23; La, 16.59. Found: C, 36.08; H, 3.52; N, 1.76; F, 27.44; La, 16.73.

Neutral Complexes. Bis(2,4-pentanedionato)beryllium(II), mp 108–109°, lit.[29] 108.5–109°, and tris(2,4-pentanedionato)scandium-(III), mp 187.5–189°, lit.[30] 188°, were prepared using standard methods.[29,30]

Nmr Chemical Shifts. Chemical shifts were determined with a Varian A-60 or A-60A spectrometer at 60.000 Mc. The magnetic field sweep of the instruments was checked against the chemical shift of a 2% (by volume) solution of benzene in carbon tetrachloride.[31]

Results and Discussion

Chemical Shifts. Proton chemical shifts for several cationic acetylacetonate complexes and anionic benzoylacetonate (bzac) and trifluoroacetylacetonate (tfac) complexes in deuteriochloroform solution are presented in Table I. Shifts for analogous neutral metal acetylacetonates are listed in Table II.

It is apparent that the methyl and ring proton (−CH=) resonances of the cationic complexes are shifted to lower fields by −0.25 to −0.54 and −0.54 to −1.37 ppm, respectively, relative to the average shifts of −2.02 ± 0.09 ppm (CH₃) and −5.47 ± 0.08 ppm (−CH=) for the neutral complexes. In the case of the methyl resonances, the low-field shifts are essentially independent of the nature of the anion and the concentration of the solutions. The −CH= shifts depend on both anion and concentration; however, these dependences are small (∼10–25 and ∼5%, respectively) compared with the over-all low-field shifts. The shifts increase as the central ion varies in the order Ge(IV) < Si(IV) < Ti(IV) < B(III); except for the position of Ti-(IV), this is the order of decreasing ionic radius.

The ring current hypothesis predicts no low-field shifts for B(acac)₂⁺ since boron uses all of its valence orbitals

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Table II. Chemical Shifts for Neutral Metal
Acetylacetonates in CDCl₃ Solution[a]

Compound	-CH=	-CH₃	Ref
Be(acac)₂	-5.63	-2.09	b
Zn(acac)₂	-5.47	-2.00	c
Pd(acac)₂	-5.42	-2.07	d
Sc(acac)₃	-5.54	-2.00	b
Al(acac)₃	-5.48	-2.00	e
Ga(acac)₃	-5.43	-2.01	e
In(acac)₃	-5.41	-2.02	e
Co(acac)₃	-5.52	-2.22	c
Rh(acac)₃	-5.47	-2.13	c
Zr(acac)₄	-5.48	-1.92	f
Hf(acac)₄	-5.46	-1.92	f
Ce(acac)₄	-5.31	-1.91	f
Th(acac)₄	-5.44	-1.93	f
Mean ± σ	-5.47 ± 0.08	-2.02 ± 0.09	

[a] Shifts for the Zr, Hf, Ce, and Th complexes refer to CHCl₃ solutions. [b] This work. [c] D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965). [d] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963). [e] A. J. Carty, D. G. Tuck, and E. Bullock, *Can. J. Chem.*, **43**, 2559 (1965). [f] T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **5**, 233 (1966).

in σ-bond formation, and there are no low-lying orbitals available for formation of π bonds. Thus, benzenoid structure IV should be of no importance and no π-electron ring currents are expected. In contrast to this expectation, the largest low-field shifts are observed for the boron complexes, which clearly demonstrates that the low-field shifts cannot be accounted for in terms of benzenoid ring currents.

The general occurrence of low-field shifts for the cationic complexes, and the dependence of the shifts on the size of the central ion, suggests that the shifts are due primarily to the charge on the ions. This view is supported by displacements of the resonances of the anionic M(bzac)₄⁻ and M(tfac)₄⁻ complexes to higher field (by +0.1 to +0.3 ppm) relative to the resonances of neutral metal benzoylacetonates[9] and trifluoroacetylacetonates.[10,32]

Electric Field Effects. The charge on the ionic complexes gives rise to an electric field which will alter the proton resonance frequencies. The chemical shift Δσ due to the electric field is given theoretically by the relation[33,34]

$$\Delta\sigma = -2.9 \times 10^{-12}E_z - 7.38 \times 10^{-19}E^2 \quad (1)$$

where E_z is the component of the electric field along the C-H bond, and E is the absolute magnitude of the electric field, both evaluated at the proton; values of the proportionality constants are those given by Musher.[34] This equation has recently been applied by Smith and Wilkins[18] to account for the chemical shifts of certain dipolar metal acetylacetonates.

In order to assess the importance of the electric field in the charged complexes, we have adopted the simplest possible model—an isolated cation or anion whose charge is located at the central metal ion. Such a point-charge model is clearly unrealistic for the anions since most of the negative charge will be on the chelate rings. However, if we approximate the distribution of charge on the rings by a spherically symmetric distribution, the electric field at the resonant protons, which are

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(33) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
(34) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

located on the exterior of the molecule, will be the same as for the point-charge model. The electric field at each proton is given by $E = qr/r^3$, where q is the charge on the ion in esu units, r is the vector extending from the central metal ion to the proton, and r is the length of this vector, the metal-proton distance, in centimeters.

Bond distances and bond angles used in calculating the electric fields are given in V and VI; unfortunately, no X-ray structures have been reported for any of the

V   VI (R=CH₃,CF₃,or C₆H₅)
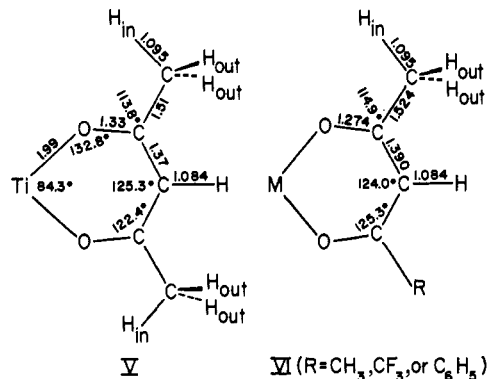
compounds in Table I. The model for Ti(acac)₃⁺(V) is based on X-ray results for [Ti(acac)₂Cl]₂O·CHCl₃.[35] Distances and angles for all other complexes (VI) were taken equal to the mean values given by Lingafelter and Braun.[3a] In all cases, we assume a planar chelate ring, a tetrahedral methyl group, and methyl and ring proton C-H distances equal to the C-H distances in methane and benzene, respectively. Following Smith and Wilkins,[18] we further assume that the methyl group is oriented as shown in V and VI, with H_{in}, the proton farthest from the ring proton, in the plane of the chelate ring, but undergoing hindered rotation about the C-C bond such that the environment of the methyl protons is averaged over the H_{in} and H_{out} sites. Therefore, the chemical shift for the methyl protons is given by $\Delta\sigma(CH_3) = \frac{1}{3}[\Delta\sigma(H_{in}) + 2\Delta\sigma(H_{out})]$. Finally, the M-O bond distances in VI are taken equal to the sum of the Pauling crystal radii,[36] an approximation which appears to be very good for metal ions having an inert gas electronic configuration.[3a]

The results of the calculations are presented in Table III wherein the calculated and observed values of Δσ are compared. Observed values of Δσ for the M(acac)ₙ⁺ complexes are taken as the difference between the observed chemical shift for the hexachloro-antimonate salt at a concentration of 1.0 g/100 ml (Table I) and the mean chemical shift for the neutral acetylacetonates (Table II). Observed Δσ values are based on salts containing SbCl₆⁻ (the largest of the anions studied) at the most dilute concentration in order to minimize contributions to Δσ from ion pairing. For the anionic M(bzac)₄⁻ complexes, observed values of Δσ are computed relative to chemical shifts for Al(bzac)₃ of -6.22 (-CH=) and -2.18 ppm (CH₃);[9] for M-(tfac)₄⁻, Δσ observed is related to mean chemical shifts of -5.97 ± 0.07 (-CH=) and -2.24 ± 0.10 ppm (CH₃) for nine neutral metal trifluoroacetylacetonates.[10,32]

(35) K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, **6**, 963 (1967).
(36) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 514.

Table III. Comparison of Calculated and Observed Chemical Shifts for Charged Metal Diketonate Complexes

Ion	Proton	r, Å	$E \times 10^{-5}$ [b]	$E_z \times 10^{-5}$ [b]	$\Delta\sigma$, ppm Calcd	$\Delta\sigma$, ppm Obsd
B(acac)$_2$$^+$	CH	3.79	3.34	3.34	−1.05	−1.04
	CH$_3$ in	4.03	2.96	0.95	−0.34	...
	CH$_3$ out	4.42	2.46	1.57	−0.50	...
	CH$_3$ av	...	...	...	−0.45	−0.52
Si(acac)$_3$$^+$	CH	4.16	2.77	2.77	−0.86	−0.61
	CH$_3$ in	4.23	2.68	0.68	−0.25	...
	CH$_3$ out	4.72	2.15	1.39	−0.44	...
	CH$_3$ av	...	...	...	−0.37	−0.26
Ge(acac)$_3$$^+$	CH	4.34	2.55	2.55	−0.79	−0.54
	CH$_3$ in	4.35	2.54	0.56	−0.21	...
	CH$_3$ out	4.87	2.02	1.30	−0.41	...
	CH$_3$ av	...	...	...	−0.34	−0.28
Ti(acac)$_3$$^+$	CH	4.51	2.36	2.36	−0.73	−0.75
	CH$_3$ in	4.38	2.50	0.37	−0.15	...
	CH$_3$ out	4.98	1.94	1.27	−0.40	...
	CH$_3$ av	...	...	...	−0.32	−0.27
Y(dik)$_4$$^-$ [a]	CH	4.87	−2.02	−2.02	0.56	0.20 (bzac)
						0.32 (tfac)
	CH$_3$ in	4.70	−2.18	−0.29	0.05	...
	CH$_3$ out	5.32	−1.70	−1.10	0.30	...
	CH$_3$ av	...	...	...	0.21	0.11 (bzac)
						0.20 (tfac)
La(dik)$_4$$^-$	CH	5.14	−1.82	−1.82	0.50	0.31 (bzac)
						0.31 (tfac)
	CH$_3$ in	4.89	−2.01	−0.19	0.03	...
	CH$_3$ out	5.55	−1.56	−1.01	0.28	...
	CH$_3$ av	...	...	...	0.19	0.16 (bzac)
						0.19 (tfac)

[a] dik = bzac or tfac. [b] In statcoulombs per centimeter.

Comparison of the calculated and observed values of $\Delta\sigma$ indicates that the electric field effect correctly predicts the sign and magnitude of $\Delta\sigma$. The fact that $\Delta\sigma$ for the methyl protons is only about half as large as for the −CH= proton is nicely accounted for by the smaller value of E_z for the methyl protons.[37] In view of the uncertainty of ca. ±0.09 ppm in the mean chemical shifts for the neutral complexes, the calculated and observed values of $\Delta\sigma$ are in good quantitative agreement, except for the ring proton resonances of Si(acac)$_3$$^+$, Ge-(acac)$_3$$^+$, and the anions, where the calculated shifts are ca. 30–45% too large. These discrepancies appear to be reasonably small in view of the crudeness of our model, the approximate bond distances and angles used in the calculations, and an uncertainty of ca. 10% in the coefficient of E_z in eq 1.[34] One can conclude that electric field effects satisfactorily account for the chemical shifts of charged metal diketonates, and there is no need to invoke benzenoid ring currents.

There is one qualitative feature of the chemical shift data which is inconsistent with the point-charge model: the large value of $\Delta\sigma$ for the −CH= proton of Ti-(acac)$_3$$^+$. Although the calculated and observed $\Delta\sigma$ (Table III) are in excellent quantitative agreement, the observed variation of $\Delta\sigma$ with central ion follows the order Ge < Si < Ti < B rather than the expected order Ti < Ge < Si < B. Assuming that the point-charge model overestimates $\Delta\sigma$ for Ti(acac)$_3$$^+$ by about the same amount as for Si(acac)$_3$$^+$ and Ge(acac)$_3$$^+$, one might have expected an observed $\Delta\sigma$ for Ti(acac)$_3$$^+$ of ca. −0.48 ppm instead of the experimental value of −0.75 ppm.

It is possible that the extra, low-field shift may be due to metal–ligand π bonding. Unlike boron, silicon, and germanium, titanium has vacant, low-energy d orbitals of principal quantum number one less than the principal quantum number of the valence shell. For Ti(acac)$_3$$^+$, therefore, resonance structure IV may well be of some importance since the titanium 3d$_\pi$ orbitals can mix with the ligand π orbitals.[38] One could, of course, attribute the extra, low-field shift to a ring current associated with this π bonding. However, as Linck and Sievers[8] have pointed out, π bonding does not necessarily imply a large ring current. In a ring containing as many heteroatoms as the metal acetylacetonate ring, the ring current may in fact be quite small. Strong evidence against a large ring current is the lack of correlation between the chemical shifts of neutral acetylacetonates and the π-bonding ability of the central ion.[11]

Another feature of metal–ligand π bonding which would explain the extra low-field shift is the transfer of positive charge to the ligand. Delocalization of acetylacetonate π electrons onto the metal ion is accompanied by delocalization of the metal ion's positive charge onto the ligand. (Electrons and positive holes change places.) If Ti(acac)$_3$$^+$ were spherical, $\Delta\sigma$ would be unaffected. However, for a real complex with three chelate rings, transfer of positive charge to the ligand atoms increases the electric field at the −CH= proton, thus increasing the low-field shift.

Ion Pairing. It has already been mentioned that the methyl resonances of the cationic complexes are independent of the anion and concentration of the solution,

(37) The main contribution to $\Delta\sigma$ arises from the E_z term in eq 1. The electric field is slightly smaller at the more distant methyl protons, but more important, E is collinear with the ring proton C–H bond, but not with the methyl C–H bonds.

(38) We will shortly report some electronic spectral evidence for metal–ligand π bonding in titanium(IV) diketonates: N. Serpone and R. C. Fay, to be submitted for publication.

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but that the ring proton signals depend on both anion and concentration. The $-CH=$ resonances shift to lower field by -0.03 to -0.13 ppm upon increasing the concentration from 1 g/100 ml to 10 g/100 ml. The concentration dependence is greatest for the smallest cation studied, $B(acac)_2^+$, and it increases with decreasing size of the anion (cf. in Table I, the series $[B(acac)_2]X$; $X = SbCl_6^-$, $AuCl_4^-$, HCl_2^-). By relating the ring proton chemical shift for a given $[M(acac)_n]X$ compound to the shift for the corresponding $[M(acac)_n]$-$[SbCl_6]$, one finds that the $-CH=$ resonances shift to lower field as the anion varies in the order $SbCl_6^- \sim AuCl_4^- < I_3^- \sim ClO_4^- < HCl_2^- < Br^- \sim Cl^-$; this is the order of decreasing anion size. Again, the effect is more pronounced, the smaller the cation.

The anion and concentration dependence can be understood in terms of ion pairing. Location of an anion near the $-CH=$ proton would increase the electric field at the proton by an amount which depends on the distance from the proton to the center of the anion; thus, $\Delta\sigma$ should become more negative as the anion size decreases. The concentration dependence of $\Delta\sigma$ reflects increasing dissociation of ion pairs with decreasing solute concentration.

Because the methyl resonances are independent of anion and concentration, it is tempting to suggest that the anion in the ion pair is located near the $-CH=$ proton rather than near the methyl groups. A simple calculation indicates, however, that the methyl resonances will be rather insensitive to ion pairing

because the electric field due to the anion is nearly perpendicular to the C–H bonds; location of the anion along the threefold axis of the methyl group gives a change in $\Delta\sigma$ of only ca. -0.02 ppm on going from $[M(acac)_n][SbCl_6]$ to $[M(acac)_n]Cl$. The anion may in fact prefer to be near the $-CH=$ proton, but our data are equally consistent with an ion pair in which there is no strongly preferred site for the anion. What one can say is that the anion is not located exclusively along the threefold axis of the octahedral complexes (or along the two C'_2 axes of $B(acac)_2^+$), since such a location predicts a positive change in $\Delta\sigma$ as the size of the anion decreases. [39]

(39) A referee has suggested that some of the variations in chemical shifts observed in this work may represent solvation effects since deuteriochloroform is known to hydrogen bond to certain metal acetylacetonates: T. S. Davis and J. P. Fackler, Jr., Inorg. Chem., 5, 242 (1966). We have recorded nmr spectra of $[B(acac)_2][SbCl_6]$ and $[Si(acac)_3][SbCl_6]$, and of the isoelectronic neutral complexes, $Be(acac)_2$ and $Al(acac)_3$, at a concentration of 10 g/100 ml of solvent in dichloromethane, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane, as well as in deuteriochloroform. The methyl group $\Delta\sigma$ values (defined here as the difference between the chemical shift for a charged complex and the corresponding isoelectronic neutral complex) are the same (± 0.01 ppm) in all four solvents. The ring proton $\Delta\sigma$ values are the same in dichloromethane, dichloroethane, and tetrachloroethane but are larger by ca. -0.1 ppm in deuteriochloroform. Similar results were obtained for $[B(acac)_2][HCl_2]$, $[Si(acac)_3]Cl$, and $[Si(acac)_3]Br$. The slightly larger CH proton $\Delta\sigma$ values in deuteriochloroform could be due to hydrogen bonding. However, variations in $\Delta\sigma$ attributable to hydrogen bonding are small compared with the total, observed $\Delta\sigma$ values (cf. Table III).

The Linear $\Delta H - \Delta\bar{\nu}_{C=O}$ Relation for Ethyl Acetate Adducts and Its Significance for Donor–Acceptor Interactions

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Abstract: A linear correlation has been found between the ethyl acetate carbonyl frequency shift upon complexation and the enthalpy of adduct formation for a series of Lewis acids. This phenomenon is discussed with respect to the energetics of adduct formation. A modified idea of the traditional reorganization energy is necessary to explain the correlation. An alternative way to look at the energetics of adduct formation is introduced using the concepts of unit basicity and unit acidity.

We have been interested in establishing quantitative correlations between changes in the spectroscopic properties of a donor or acceptor upon coordination and the gas-phase (or equivalent) enthalpy of adduct formation, ΔH_f. Successful correlations have been reported between the change in the O–H stretching frequency of phenol upon complexation, $\Delta\bar{\nu}_{OH}$, and ΔH_f for 1:1 adducts with a whole series of donors,[2,3] and another between the change in the tin–proton coupling constant of $(CH_3)_3SnCl$ upon adduct formation

and ΔH_f.[4] A theoretical rationalization for the phenol correlation has been presented.[5] It is of interest to extend these correlations to a donor molecule which undergoes a pronounced spectral change on complexation.

In a series of recent articles, Lappert[6] has used the shift in the carbonyl stretching frequency of ethyl acetate to investigate the acceptor properties of various Lewis acids. By making the assumption that the stronger Lewis acid will shift the carbonyl infrared stretch more upon complexation, he found the same qualitative trends in acidity along a series of Lewis

(1) National Science Foundation Predoctoral Fellow, abstracted in part from the Ph.D. thesis of D. G. Brown.

(2) M. D. Joesten and R. S. Drago, J. Am. Chem. Soc., 84, 2037, 2696, 3817 (1962).

(3) T. D. Epley and R. S. Drago, ibid., 89, 5770 (1967).

(4) T. F. Bolles and R. S. Drago, ibid., 88, 3921 (1966).

(5) K. F. Purcell and R. S. Drago, ibid., 89, 2874 (1967).

(6) (a) M. F. Lappert, J. Chem. Soc., 542 (1962); (b) M. F. Lappert and J. K. Smith, ibid., 5826 (1965).