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# $\pi$-Interaction in Metal $\beta$-Ketoenolates

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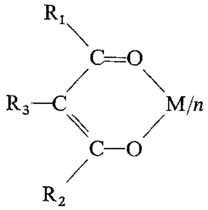
The available data (supplemented where necessary) on the electronic, nuclear magnetic resonance and vibrational spectra of metal $\beta$-ketoenolates has been analysed to assess the relative contributions of donor and acceptor metal-ligand $\pi$-bonding in the first transition period metal (III) $\beta$-ketoenolates. The effects of the metal ion and the ligand substituent on the $\pi$-interaction in the $\beta$-ketoenolate ring are discussed in terms of established theoretical concepts.

Die bekannten Daten (ergänzt, falls notwendig) der elektronischen und kernmagnetischen Resonanz sowie der Schwingungsspektren von Metall-$\beta$-ketoenolaten wurden analysiert, um die relativen Beiträge von Donor- und Akzeptor (Metall-Ligand) $\pi$-Bindung in Metall(III)ketoenolaten der ersten Übergangsperiode zu ermitteln. Die Einwirkung des Metallions und des Ligandsubstituenten auf die $\pi$-Bindung im $\beta$-Ketoenolatring werden diskutiert auf der Grundlage von bekannten theoretischen Prinzipien.

L'examen des résultats antérieurement publiés (supplementés ou nécessaire) des spectres électroniques, résonance nucléaire magnetiques et vibrationnel nous a amenés à preciser les contributions relatifs de liaison-$\pi$ donneur et accepteur entre métal et ligand de la première période transitionelle métal(III) $\beta$-kétoénolates. Les effects de l'ion métallique et du ligand substituent exercés sur l'interaction-$\pi$ dans le noyau $\beta$-kétoénolate sont discutés selon les idées théoriques déjà établies.

## Introduction

There is some confusion in the literature on the nature and extent of $\pi$-interaction in the chelate ring of metal $\beta$-ketoenolates. Thus the position of the acetylacetonate ion in the spectrochemical series (close to water) implies weaker metal-ligand $\pi$-bonding than the relatively high $\pi - \pi^*$ transition energies would suggest. Since a fairly extensive literature now exists on the spectroscopy of these complexes, we have examined the extent to which the combined data provides information on the effects of the metal ion and substituent on $\pi$-interaction in the chelate ring. The discussion relates to the compounds (I) in which the substituents $R_1$, $R_2$, $R_3$ are hydrogen, alkyl, aryl, trifluoromethyl or halogen groups.



(I)

## Effect of the Metal Ion

Barnum [1] has studied the electronic spectra of the first transition period metal(III) acetylacetonates (I; $R_1 = R_2 = CH_3$; $R_3 = H$; $n = 3$) with assignments based on a Hückel LCAO-MO treatment [2]. The derived energy levels are shown in Fig. 1. The occupied $\pi_3$ and unoccupied antibonding $\pi_4^*$ MO's are both energetically suitable for overlap with the metal ion $d_\varepsilon$ orbitals so that both donor ($M - \pi^*$) and acceptor ($\pi - M$) $\pi$-bonding are possible. The theoretical treatment shows that the $\pi_3$ orbitals of the acetylacetonate ion are depressed while the $\pi_4^*$ orbitals are relatively unaffected by $\pi$-interaction so that acceptor $\pi$-bonding is considered to provide the greater contribution to the total $\pi$-bonding (except for the Co(III) complex). Furthermore the treatment shows that increased $\pi$-interaction will increase the splitting between the $\pi_3$ and $\pi_4^*$ levels and thus raise the $\pi - \pi^*$ transition energy.

In redetermining the spectra of the acetylacetonates we find essential agreement with Barnum's data. In terms of the MO treatment the bathochromic shift of the $\pi - \pi^*$ band through the series of transition ions (Fig. 2) implies that the $\pi$-interaction is dependent on the $d$-orbital population but the increments are irregular, a plateau being realised for the complexes of Cr(III), Mn(III) and Fe(III). This feature suggests that other $\beta$-ketoenolate systems warranted examination. Fig. 2 shows that these systems do not conform to a simple dependence on $d$-orbital population, the general order being Co > Cr ~ Fe > Mn ~ V. We may

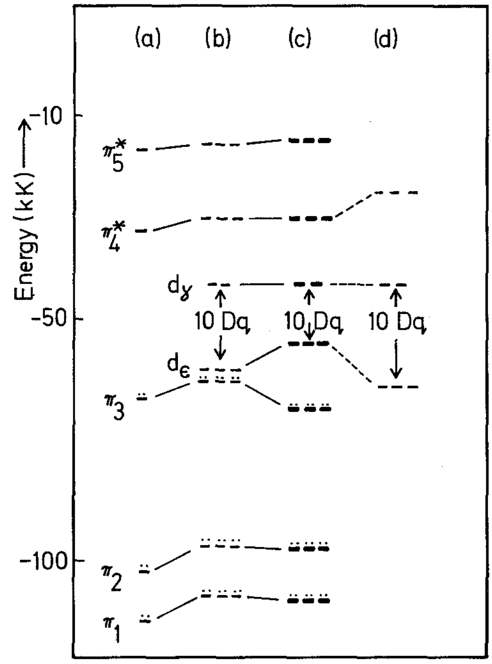


Fig. 1. Molecular orbital levels of (a) acetylacetonate anion ($AA^-$); (b) $[M(AA)_3]$ without $\pi$-bonding; (c) $[M(AA)_3]$ with $\pi$-bonding; (d) effect of strong metal-ligand donor $\pi$-bonding

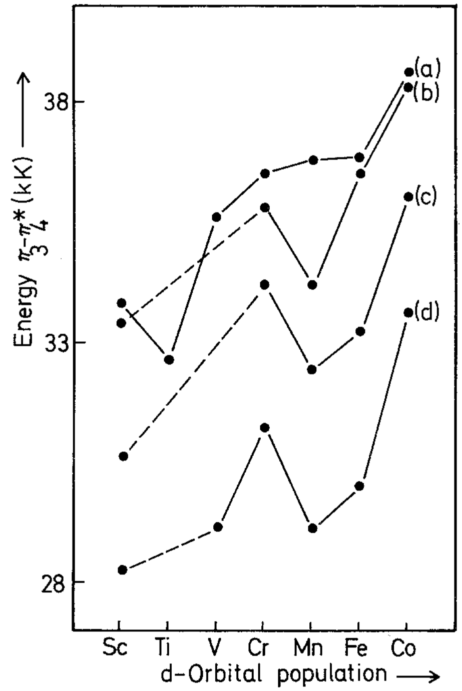


Fig. 2. Relationship between $\pi_3$-$\pi_4^*$ transition energy and *d*-orbital population for transition metal(III) complexes of (a) acetylacetone; (b) trifluoroacetylacetone; (c) benzoylacetone; (d) dibenzoylmethane

express this order by stating that the total $\pi$-interaction increases with *d*-orbital population except that it is particularly large in the Cr(III) and particularly small in the Mn(III) complexes.

The NMR spectra of the paramagnetic first transition series metal(III) acetylacetonates [5] also lead to conclusions about the metal ion dependence of the $\pi$-interaction. The shifts were concluded to be largely contact in origin and were interpreted in terms of delocalization of spin in ligand $\pi$-MO's. Spin density distributions calculated by McLachlan's MO treatment [12] yields the interpretation that donor $\pi$-bonding would result in a large low field shift for the $CH_3$ signal. Interpretation of the direction and extent of the CH proton shift is somewhat less conclusive except that a large high field shift implies ligand to metal $\beta$-spin transfer. The results (Table 1) enabled Eaton [5] to conclude that donor $\pi$-bonding is a maximum at Ti(III) and diminishes monotonically through Fe(III) which exhibits the maximum acceptor $\pi$-bonding.

The results of the two spectroscopic techniques show that conclusions with respect to the direction and extent of the $\pi$-interaction may be reached for specific metal ions. Thus the Ti(III) complex exhibits the maximum of donor $\pi$-bonding (NMR) but the minimum total $\pi$-interaction (UV) suggesting that the general level of donor $\pi$-bonding is relatively small except for complexes of Co(III). This latter ion is unique among the first row transition metal(III) ions in having a spin paired configuration. The filled $d_\varepsilon$ level ensures that only donor $\pi$-bonding is possible. The relatively high $\pi - \pi^*$ transition energy implies that the donor

Table 1. *Electronic, nuclear magnetic resqnance and infrared spectral data on first row transition metal(III) acetylacetonates*

| Parameter | Sc | Ti | V | Cr | Mn | Fe | Co |
|---|---|---|---|---|---|---|---|
| $\pi_3 - \pi_4^{*\,a}$ (kK) | 33.8 | 32.6$^e$ | 35.6 | 36.5 | 36.8 | 36.8 | 38.6 |
| $d_\varepsilon - \pi_4^{*\,a}$ (kK) | — | 25.7$^e$ | 27.3 | 29.8 | 31.7 | 28.7 | 30.9 |
| $10\,Dq^b$ (kK) | — | 13.5$^f$ | 18.0 | 18.1 | 17.0 | 16.4 | 21.0 |
| $\Delta\nu(CH_3)^c$ (c.p.s.) | — | −3500 | −2744 | −2320 | −1505 | −1243 | — |
| $\Delta\nu(CH)^c$ (c.p.s.) | — | — | −2404 | — | −1085 | +1644 | — |
| $\nu$C–O$^d$ (cm$^{-1}$) | 1580 | 1565 | 1571 | 1574 | 1593 | 1575 | 1580 |
| $\nu$M–O$^d$ (cm$^{-1}$) | 542 | 556 | 572 | 595 | 570 | 550 | 637 |

[a] Electronic spectra in chloroform except for Ti(III) complex (in ethanol).

[b] Ref. [13].

[c] Ref. [5]. NMR contact shifts (at 60 Mc.p.s.) in c.p.s. from TMS; solvent: $CDCl_3$ except for Ti(III) complex (in $C_6D_6$).

[d] Ref. [9]. Infrared stretching frequencies for nujol mulls.

[e] Ref. [1].

[f] Considered [13] to be anomalously low.

$\pi$-bonding is strong, a feature which is also consistent with the relatively high value [13, 18] of the crystal field splitting parameter, 10 Dq, for the Co(III) complexes (donor $\pi$-bonding increases 10 Dq while acceptor $\pi$-bonding diminishes it). The relatively high M–O stretching frequency ($\nu$M–O) exhibited by each of the Co(III) complexes [9] is also consistent with strong $\pi$-bonding but does not require it since $\nu$M–O reflects the total bonding, $\sigma$ and $\pi$.

The NMR data [5] shows Mn(III) to occupy a position of diminished donor $\pi$-bonding while the generally low $\pi - \pi^*$ transition energies suggest that the total $\pi$-interaction is also relatively small in complexes of this ion. In fact the IR spectra [9] indicate that the metal-ligand bonding in the Mn(III) complexes is fairly ionic since $\nu$C–O is relatively high, a characteristic of the $\beta$-ketoenolates of electropositive ions. The relatively low value of 10 Dq for the acetylacetonate [13] is also consistent with ionic character in the Mn–O bond.

Fe(III) acetylacetonate has a maximum of acceptor and a minimum of donor $\pi$-bonding according to the NMR data. These features would jointly depress 10 Dq. In fact Fe(III) acetylacetonate exhibits an appreciably low value of 10 Dq [13].

The Cr(III) complexes occupy an interesting position of intermediate donor and acceptor $\pi$-bonding strength. The joint contribution yields a relatively strong total $\pi$-interaction and an intermediate magnitude of 10 Dq.

We conclude therefore that the combined NMR and electronic spectral data enable a qualitatively acceptable picture of the relative contributions of donor and acceptor $\pi$-bonding to the total $\pi$-interaction in transition metal(III) $\beta$-ketoenolates to be made. The conclusions are summarized in Table 2.

Although there is general agreement [1, 4] with respect to the assignment of the $\pi - \pi^*$ band in the electronic spectra of metal $\beta$-ketoenolates, the assignment of the $d_\varepsilon - \pi^*$ transition given by Barnum [1] is not unanimously accepted [11]. We will use the conclusions in Table 2 and the data in Table 1 to support Barnum's assignment. Donor $\pi$-bonding lowers the $d_\varepsilon$ level and increases 10 Dq while acceptor $\pi$-bonding raises the $d_\varepsilon$ level and decreases 10 Dq. Therefore we would

Table 2. *Qualitative comparison of donor, acceptor and total $\pi$-interaction in first row transition metal (III) $\beta$-ketoenolates*

| Ion | Relative extent of $\pi$-interaction | | |
|---|---|---|---|
| | Donor | Acceptor | Total[a] |
| Ti(III) | strong | weak | weak |
| V(III) | strong | weak | weak |
| Cr(III) | moderate | moderate | strong |
| Mn(III) | weak | weak | weak |
| Fe(III) | weak | strong | moderate |
| Co(III) | strong | absent | strong |

[a] Based on the consideration that acceptor $\pi$-bonding provides the major contribution to the total $\pi$-interaction

expect that the correctly assigned band would exhibit a bathochromic shift with increase in 10 Dq. Using Barnum's assignment this is observed except for the Mn(III) complex for which we have suggested the Mn–O bonding to be relatively ionic. This conclusion is of course subject to the condition that the $\pi_4^*$ level is relatively unaffected, a condition which is entirely in accord with the results of the LCAO-MO treatment.

We are indebted to a referee for suggesting some elaboration of the deficiencies implicit in the Hückel MO treatment of metal(III) acetylacetonates. The assumption of an almost identical diagonal element of 3*d*-electron energy between Sc(III) and Co(III) yields calculated energy levels which are generally consistent with chemical observation but not in the case of Mn(III) and probably not in the case of Co(III). For both of these ions, the order of energy levels yielded by the theoretical treatment is $d_\varepsilon < \pi_3$, i.e. Mn(III) should be reduced by acetylacetone. This does not occur. The same argument cannot be applied to Co(III) because the $d_\varepsilon$ level is filled in this ion. Barnum [2] has mentioned these points and has pointed out that the margin of error in his calculations is sufficiently large that the calculated orders of the $d_\varepsilon$ and $\pi_3$ levels could well be reversed. Furthermore, the theoretical treatment leads to the energy order $d_\gamma < \pi_4^*$ for all ions. This must at least obtain for the high spin $d^4$ and $d^5$ ions otherwise they would be oxidized (which also does not occur). Eaton [5] has also emphasized that the Hückel MO treatment fails to take into account the electronic correlations which can give rise to negative spin densities in the acetylacetonate system. It is for this reason that McLachlan's modification [12] (in which the $\alpha$- and $\beta$-spins are allowed to occupy separate Hückel-type MO's) was used to predict the contact shifts which agree well with experimental observation. With the reservations necessary in the absence of more refined theoretical models, the measure of support provided by the three spectroscopic techniques discussed here must be considered very heartening.

## Effect of the Ligand Substituent

Quite apart from the effect of the metal ion, the $\pi$-interaction in the chelated $\beta$-ketoenolate ring will be influenced by the type of ligand substituent present. The effect of substitution of aromatic systems by alkyl and aryl groups has been treated by Coulson [3] on a MO model. Introduction of a substituent at the

$r^{\text{th}}$ atom of a cyclic conjugated system causes a change in the energy of the $\psi_i \to \psi_j$ transition given by

$$\delta(h\nu) = (c_{jr}^2 - c_{ir}^2)\,\delta\alpha_r$$

where $c_{jr}$ and $c_{ir}$ are the coefficients of the $r^{\text{th}}$ AO in the higher and lower energy MO's and $\delta\alpha_r$ is the change in the $r^{\text{th}}$ atom Coulomb integral. Red and blue shifts resulting from substitution at a specific ring carbon are interpreted in terms of the sign of $\delta\alpha_r$.

A similar treatment [4] of the effects of substitution on the $\pi-\pi^*$ transition energies of a series of Cr(III) $\beta$-ketoenolates led to the view that the mesomeric effect governs the $\pi$-interaction as it does in aromatic systems. Here we will consider an interpretation of the shifts in terms of available substituent parameters.

The Hammett substituent constant [8, 10] is commonly employed as a measure of the sign and magnitude of the electron density induced by a substituent (relative to hydrogen) at the reaction site of an aromatic system. Since this constant is the resultant of the inductive and mesomeric effects (both of which may affect the $\pi$-electron density of the chelate ring) and since the Hammett constants are strictly applicable only to aromatic systems, it will be more appropriate to consider these effects separately. Recently Swain and Lupton [16] have shown that a substituent effect ($\sigma$) may be expressed in the form

$$\sigma = f\mathscr{F} + r\mathscr{R}$$

where $\mathscr{F}$ and $\mathscr{R}$ are the inductive (field) and mesomeric (resonance) effects and $f$ and $r$ are the relative weightings of each. $\mathscr{F}$ and $\mathscr{R}$ are intrinsic properties of the isolated substituents while $f$ and $r$ vary according to the nature of the ring system and the position of substitution.

Table 3. *Effect of substituents on $\pi-\pi^*$ transition energies of $\beta$-ketoenolates (formula I)*

| Substituents | | | Substituent parameter | | $\pi_3-\pi_4^*$ transition energy (kK) in chloroform[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_1$ | $R_2$ | $R_3$ | $\sum\mathscr{R}$ | $\sum\mathscr{F}$ | $M$ = Sc | Cr | Mn | Fe | Co | Al | Cu | K |
| | | | | | $n$ = 3 | 3 | 3 | 3 | 3 | 3 | 2 | 1 |
| H | H | H | 0 | 0 | — | 35.5[b] | — | — | — | — | — | — |
| $CH_3$ | H | H | −0.141 | −0.052 | — | 36.0[b] | — | — | — | — | — | — |
| $CH_3$ | $CH_3$ | H | −0.282 | −0.104 | — | 36.5 | — | — | — | — | — | — |
| $C_6H_5$ | $C_6H_5$ | H | −0.176 | +0.278 | 28.2 | 31.2 | 29.1 | 30.0 | 33.6 | 28.6 | — | 29.4 |
| $C_6H_5$ | $CH_3$ | H | −0.229 | +0.087 | 30.6 | 34.2 | 32.4 | 33.2 | 36.1 | 31.3 | — | 32.6 |
| $CH_3$ | $CH_3$ | H | −0.282 | −0.104 | 33.8 | 36.5 | 36.8 | 36.8 | 38.6 | 35.2 | — | 36.2 |
| $CF_3$ | $CF_3$ | H | +0.372 | +1.262 | — | 33.8 | — | 36.1 | — | 33.0 | 32.3[c] | 33.0 |
| $CF_3$ | $CH_3$ | H | +0.045 | +0.579 | 33.4 | 35.8 | 34.2 | 36.5 | 38.3 | 34.4 | 33.4[c] | 34.2 |
| $CH_3$ | $CH_3$ | H | −0.282 | −0.104 | 33.8 | 36.5 | 36.8 | 36.8 | 38.6 | 35.2 | 33.8[c] | 36.2 |
| $CH_3$ | $CH_3$ | Cl | −0.443 | +0.586 | — | — | — | 36.1[d] | 38.8[d] | 34.5[d] | 37.3[d] | — |
| $CH_3$ | $CH_3$ | Br | −0.458 | +0.623 | — | — | — | 36.0[d] | 37.6[d] | 32.8[d] | 33.7[d] | — |
| $CH_3$ | $CH_3$ | I | −0.479 | +0.568 | — | — | — | 35.7[d] | 36.4[d] | — | — | — |

[a] Except for K(I) complexes (in methanol).

[b] Ref. [4]. — [c] Ref. [6]. — [d] Ref. [14].

Assuming additivity of the substituent effects the calculated values of $\sum\mathscr{R}$ are given in Table 3. The $\pi-\pi^*$ transition energies exhibit no regular correlation with $\sum\mathscr{R}$ over the whole range of substituents but some conclusions are possible if the complexes are divided into three categories: effect of substitution of H by $CH_3$; of $C_6H_5$ by $CH_3$; and of $CF_3$ by $CH_3$. With this division it is observed that within each triad the $\pi-\pi^*$ transition energies exhibit the expected increase with greater mesomeric electron release of the substituents. The positive values of $\sum\mathscr{R}$ for the tri- and hexa-fluoroacetylacetonates implies that the joint influence of the two substituents in these complexes is electron withdrawing. Under these circumstances the $\pi-\pi^*$ transition energies for these complexes seem rather high. However the $CF_3$ group is unique among those studied in that the inductive effect causes a displacement of the $\sigma$-electron density towards fluorine and $\pi$-electron density towards carbon [15]. Clearly the latter governs the $\pi-\pi^*$ transition energies and would be expected to raise them. This feature illuminates the limitations of using substituent parameters in correlations with electronic transition energies orginating in $\pi$-MO's. The sign and magnitude of $\mathscr{R}$ represents the total ortho-para directing effect of the substituent in an aromatic system and gives no indication that the $\sigma$- and $\pi$-electron flow may be in opposite directions. In this connection it is to be noted that although correlations between substituent-induced $\pi-\pi^*$ shifts ($\Delta\nu$) and Hammett $\sigma$-values have previously been established for aromatic systems, anomalies are observed for certain substituents. Thus Gerson and Heilbronner [7] have shown that substituents with a positive value of $(\sigma-\sigma')$ do not conform to the linear relationship between $\sigma$ and $\Delta\nu$ observed for other substituents in phenyl-azo-azulenes. $(\sigma-\sigma')$, the resonance polar effect in Taft's [17] terminology, is positive for those substituents which, like $CF_3$, exhibit a second order inductive effect.

We have assumed that, by analogy with conjugated aromatic systems, the mesomeric effect predominates in determining the $\pi-\pi^*$ transition energies. This is not an obvious result of the trend to higher energies with increased mesomeric effect as indicated by the magnitude of $\sum\mathscr{R}$ for each triad in Table 3 since it transpires that $\sum\mathscr{F}$ fortuitously exhibits the same trends as $\sum\mathscr{R}$ for the examples studied. However the predominance of the mesomeric effect is suggested by the remarks made on the $CF_3$-substituted complexes. Further support is available from a comparison of the $\pi-\pi^*$ energies [14] of the halogen-substituted complexes (Table 3). The halogens are inductively electron withdrawing and mesomerically electron releasing. Iodine has the greatest mesomeric effect but yields the lowest $\pi-\pi^*$ transition energy. The relative magnitudes of $(\sigma-\sigma')$ for the halogens [17] show that iodine provides the maximum $\pi$-electron release by the resonance polar effect and it is clear therefore that the halogens resemble the trifluoromethyl group in that this effect governs the nett $\pi$-interaction.

A noteworthy feature of the results in Table 3 is the qualitative similarity of the substituent dependence of the $\pi-\pi^*$ transition energies for both transition and non-transition metal complexes. Calculation of the mean shift in the $\pi-\pi^*$ energy per unit of the resonance parameter ($\mathscr{R}$) on replacement of phenyl and trifluoromethyl groups by methyl groups (Table 4) shows that the $\pi-\pi^*$ band is generally more sensitive to the substituent in the non-transition complexes. The Mn(III) complexes also exhibit a high degree of substituent sensitivity, a feature

Table 4. *Comparison of the substituent sensitivity of the $\pi_3 - \pi_4^*$ transition energies in metal $\beta$-ketoenolates*

| Substituent replaced | Substituent introduced | Mean shift in $\pi_3 - \pi_4^*$ transition energy per unit $\mathscr{R}$ (kK) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Sc | Cr | Mn | Fe | Co | Al | Cu | K |
| $C_6H_5$ | $CH_3$ | −53 | −51 | −74 | −64 | −47 | −62 | – | −64 |
| $CF_3$ | $CH_3$ | − 0.6 | − 2.1 | − 3.8 | − 0.6 | − 0.4 | − 1.6 | −1.2 | − 2.3 |

which is consistent with our earlier suggestion that there is a degree of ionic character in the Mn–O bond. Furthermore the minimum substituent sensitivity is exhibited by the complexes of Co(III) for which the maximum of metal-ligand donor $\pi$-bonding is indicated.

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