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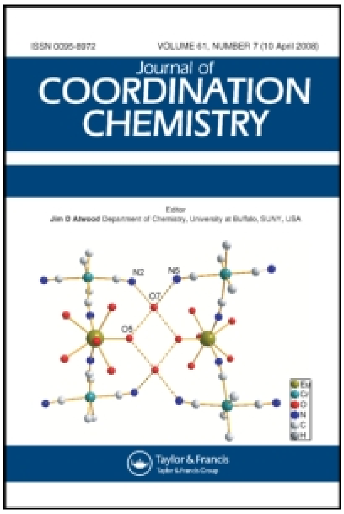

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SHORT COMMUNICATION
Substituent Effects on Molecular Ionization Potentials XIII. Copper Acetylacetonates

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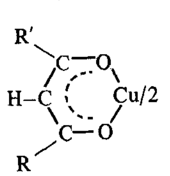
In this paper we report the first correlation of molecular ionization potentials of metal coordination complexes with the substituent constants. Recently we have shown that the ionization energies of the alcohols,[1] ethers,[2] amines,[3] thiols,[4] thioethers,[5] disulfides,[6] alkenes,[7] alkynes,[8] alkyl halides,[9] carboxylic acids,[10] ketones,[11] nitroalkanes,[12] and nitriles[12] are linear functions of the inductive substituent constants, σ_I, and the polar substituent constants, σ^*. This permits one to calculate by means of a simple single-parameter equation, to a good approximation, values of the ionization potentials of compounds which yield a low abundance of the primary cation radical, or are difficult to obtain in a purified state, or vaporize only with decomposition.

We now demonstrate that the ionization energies of alkyl substituted bis-(β-keto enolate) complexes of Cu(II)



are a linear function of Hammett's substituent constants.[13] The first ionization energy of these chelates corresponds to the removal of an electron from the highest occupied molecular orbital,[14,15] presumably from the π-system or from the unpaired electron in the d_{xy} orbital[16] of Cu, remaining after formation of its hybrid $d_{x^2-y^2}\, s\, p_x p_y$ orbitals. This electron is, according to ligand field theory, in an e_g orbital in a field of D_{2h} symmetry. The gas-phase expulsion of an electron from these paramagnetic quasi-aromatic compounds[17] results, presumably, in a diamagnetic cation.

It is quite obvious that electron releasing alkyl groups should increase the electron density of the heteroaromatic ring and thereby facilitate electron removal, whereas electron-withdrawing groups should increase the requisite ionization energy.[18]

It is seen from the position of the substituents in the above formulation that the appropriate substituent constant should be the σ_m parameter derived originally for *meta* substituents on the benzene ring,[19] and for those para substituents which introduce no additional resonance effects.[20] It should be noted that σ_m, like σ_I,[21] is a measure of the inductive influence of a substituent.[20] Table I presents the $\Sigma\sigma_m$ values together with the experimentally observed[22] electron impact ionization potentials (E_I) for a series of seven of the copper II chelates.

TABLE I

Compound number	Ring substituents	$\Sigma\sigma_m$[a]	E_I(eV)[b] (Exptl.)	E_I(eV) (Eq. 2)
1	CH_3,CH_3	−0.12	7.75	7.70
2	CH_3,C_2H_5	−0.14	7.68	7.68
3	CH_3,$CH(CH_3)_2$	−0.20	7.61	7.62
4	CH_3,$C(CH_3)_3$	−0.26	7.59	7.56
5	CH_3,CF_3	+0.84	8.61	8.66
6	CF_3,CF_3	+1.80	9.68	9.62
7	$\left\{\begin{matrix} CH_3CH_3 \\ CF_3,CF_3 \end{matrix}\right\}$[c]	+0.84	8.65	8.66
8	H,H	0	[d]	7.82
9	H,CH_3	−0.06	[d]	7.76

[a] σ_m values from Ref. 13 and 19: Me = −0.03; Et = −0.04; t-BU = −0.10; CF_3 = +0.45; from Ref. 23: iPr = −0.07.

[b] E_I values from Ref. 22.

[c] Mixed ligands, one having two CH_3's and the other two CF_3's.

[d] Experimental E_I value not yet available.

A good correlation is shown in Figure 1 where the E_I values are plotted *vs* $\Sigma\sigma_m$. The equation for the regression line is given by the following:

$$E_{Cu\text{-}R} = E_{Cu\text{-}H} + a_m\, \Sigma\sigma_m \qquad (1)$$

The slope, a_m, is found to be 1.00 and the value E_{Cu-H}, which corresponds to the bis-Cu chelate of malonaldehyde, $CH_2(CHO)_2$, is by interpolation (Figure 1) 7.82 eV, and therefore we have

$$E_{Cu-R} = 7.82 + 1.00\,\Sigma\sigma_m, \qquad (2)$$

which has $r = 0.999$ with a Std. error of 0.04 eV.

This correlation indicates that the effect of alkyl substituents on the electron density in the chelate ring and at the Cu atom is primarily an inductive one, and lends support to the view that these chelates behave as heteroaromatic compounds.[17] It should be noted that the plot of E_I *vs* $\Sigma\sigma_I$ results in a curve which is concave upward.

In the last column of Table I we show a comparison between the experimentally obtained ionization energies and those values of E_I calculated by means of Eq. (2). The agreement is seen to be excellent. A calculated value is also given for the Cu chelates of malonaldehyde, $CH_2(CHO)_2$, and formyl acetone, CH_3COCH_2CHO.

Although the a_m constant has units of energy (eV), it is analogous to the reaction constant, ρ_m, and reflects the susceptibility of the reaction site, the π-system or the e_g copper electron to substituent effects. The a_m value of 1.00 obtained here may be compared to the corresponding a_m value of E_I's of monoalkylbenzenes which is found[24] to be 2.00, exactly twice that observed here for the Cu acetylacetonates.

It is interesting to note that replacing the CH_3 of toluene by CF_3 increases[25] the E_I by 0.86 eV, exactly the same increase observed when all four methyl groups of the $Cu(acac)_2$ ligands are replaced by trifluoromethyls. When CF_3 replaces H of benzene the E_I is increased[25] by 0.43 eV, and when CF_3 groups replace the four hydrogens of the Cu malonaldehyde complex the E_I is increased by 1.80 eV, or 0.45 eV/CF_3 group. This surprising agreement constitutes further evidence for the similarity of the π-systems of benzene and β-ketoenolate complexes.

The unpaired d_{xy} Cu electron[26] is the one most probably expelled from its e_g orbital, which is antibonding[26,27] and possibly delocalized[28] over the entire π-system, encompassing the Cu atom and both coplanar chelate rings.

This idea is supported by the fact that in the correlation reported herein, we have given equal weight to all four substituents ($\Sigma\sigma_m$), and by the fact that two CF_3 groups replacing two CH_3 groups, whether on one ring or both gives rise to essentially the same E_I (8.65 eV *vs* 8.61 eV) (Table I). This was also noted by Holtzclaw et al.[22] in their paper in which the experimental ionization potentials for these compounds were first reported, and is also in accord with the view expressed by Pearson *et al.*[29] that ionization of acetylacetonates involves an orbital spread over the ligand. Furthermore, we cite evidence from NMR data on other paramagnetic acetylacetonates in which the spin density of the unpaired electron is definitely delocalized and finds its way to an extent of around 10% into the spin density of the para H atoms, shifting the resonance frequency compared to the diamagnetic complexes.[30] Since there are eleven atoms in the 2-ring system of the Cu chelate, one might assume that approximately 9–10% of the spin density resides at each of the atoms in the rings.

On the other hand, there is also evidence that the site of electron loss is at the Cu atom: the fact that the correlation is obtained with the meta substituent constants, that all four substituents in the rings were given equal weight, and that the only atom equidistant from all the substituents is the Cu atom; the fact that the a_m value is only half of that obtained in the benzene correlation indicates that the reaction site is relatively distant from the substituents (compare $a_I = 28.0$[2] for $R_2\ddot{O}$: but 14.0[11] for $R_2C=\ddot{O}$:, where the electron in both cases is lost from a non-bonding oxygen lone pair); the fact that substitution of Cu for the enol H atom of acetylacetone ($E_I = 8.87$ eV)[29] *lowers* the E_I, whereas a higher value would be expected if a ligand electron were lost, since Cu^{++} withdraws electron density from the ring.

Finally, additional evidence that the metallic center might be the site of electron loss can be adduced from the oxidation of metallocenes and metal arenes where the ferrocenium, nickelocenium and *bis*-benzene chromium cations are thought to have the positive center at the metal atom. This view is also supported by the analogous reaction of photo-ionization of chlorophyll where, in the "photoelectric" theory of photosynthesis, much evidence has been obtained for the central Mg atom as the site of initial electron loss.[31]

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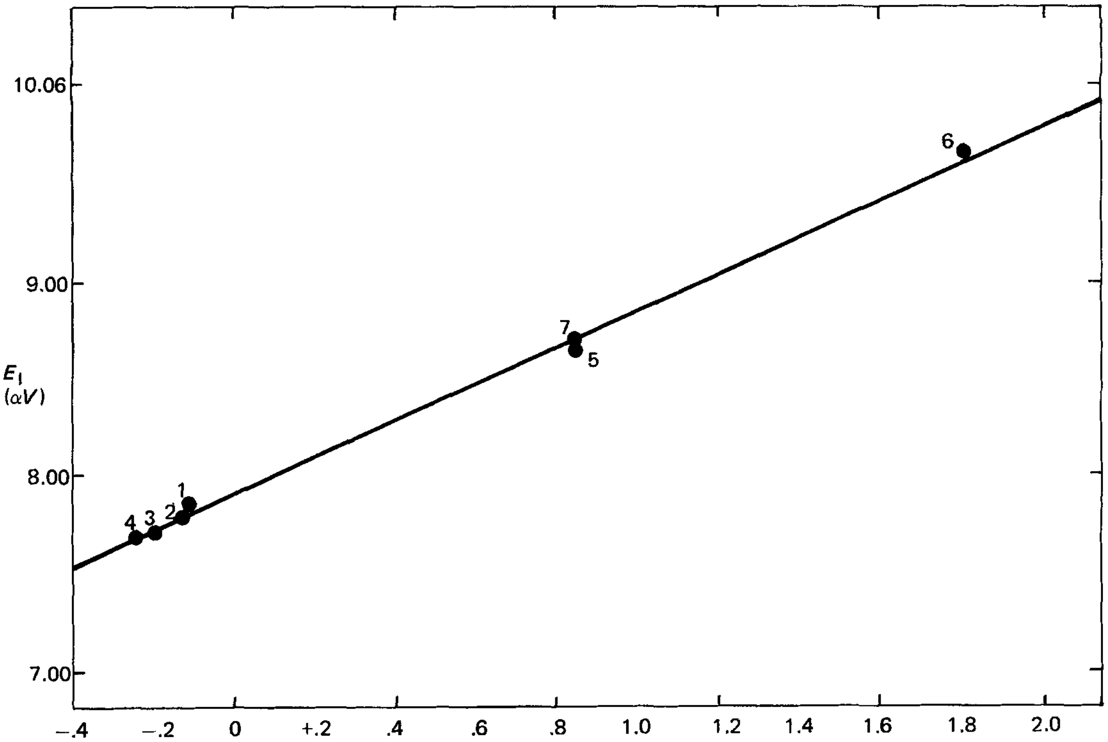

FIGURE 1 A plot of the ionization potentials of various substituted copper acetylacetonates *vs.* the sum of the *meta* substituent constants of the substituted groups.

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