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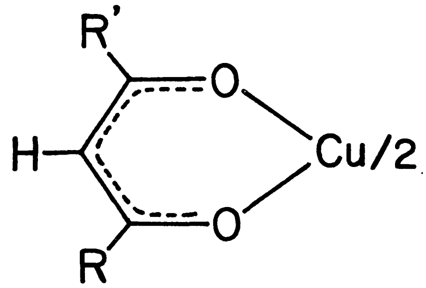
THE CORRELATION OF THE ESR PARAMETERS OF VARIOUS β-DIKETONE CHELATES OF COPPER(II) WITH THE pK_a OF THE LIGANDS

Hiroshi YOKOI and Takashi KISHI
Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai 980

All the ESR and related parameters of various β-diketone chelates of copper(II) in toluene have been recognied to correlate with the pK_a of the ligands. Results indicate that both of the σ and π coordination bondings of the complexes become more covalent as the pK_a values increase.



I

The properties of the complexes I are largely dependent upon the properties of the substituents, R and R'. A series of the complexes I with many different kinds of R and R', accordingly, are suitable for the fundamental study of the nature of coordination bondings. In this study, such complexes in toluene were thoroughly investigated by ESR and visible absorption measurements.

The complexes employed here are listed in Table 1, together with the pK_a values of the ligands[1)] and the stability constants (β_2) of the complexes.[2)]

ESR spectra were recorded at 298 and 77°K with a Hitachi 771 X-band ESR spectrometer for the 1.0 X 10^{-2} M toluene solutions of the complexes except for bis(acetylacetonato)copper(II), for which a nearly saturated solution was used owing to its limited solubility in toluene. Two of the ESR spectra measured at 77°K are shown in Fig. 1. All the other spectra were quite similar in line shape to those shown in the figure. In each of the spectra a large absorption line at the highest field is due to the extra hyperfine structure of M_I = 3/2. Accordingly, all the observed ESR line shapes can be regarded as a nearly axial type. The visible absorption spectra of the same sample solutions were measured at room temperature with a Cary 14 spectrophotometer using 10 and 40 mm quartz cells; several spectra are shown in Fig. 2. They all have apparently two absorption peaks, and the corresponding energies, which are denoted by ΔE_1 and ΔE_2, were approximately determined by the Gaussian curves.

Assuming D_{4h} symmetry and a $d_{x^2-y^2}$ ground state for the β-diketone chelates of copper(II), the g values are expressed as follows;[3)]

$$g_{/\!/} = 2 - \frac{8\lambda k_{/\!/}^2}{\Delta E_{xy}} \quad \text{and} \quad g_{\perp} = 2 - \frac{2\lambda k_{\perp}^2}{\Delta E_{xz}} \qquad (1)$$

Table 1. β-Diketones and Their Copper(II) Complexes

Ligand (LH)	R	R'	No. of CuL_2	pK_a [a] of LH	β_2 [a] of CuL_2
Dipivaloylmethane	$C(CH_3)_3$	$C(CH_3)_3$	1	15.9	
2-Acetylcyclohexanone[b]			2	14.1	23.51
2,6-Dimethyl-3,5-heptanedione	$CH(CH_3)_2$	$CH(CH_3)_2$	3	13.94	
Benzoylacetone	phenyl	CH_3	4	12.85	23.01
2-Thenoylacetone	2-thienyl	CH_3	5	12.35	28.38
2-Furoylacetone	2-furyl	CH_3	6	(11.8)[c]	
Acetylacetone	CH_3	CH_3	7	12.70	14.95
3-Benzoyl-1,1,1-trifluoroacetone	pheny	CF_3	8	9.14	18.8
2-Thnoyltrifluoroacetone	2-thienyl	CF_3	9	9.1	19.0
1,1,1-Trifluoroacetylacetone	CF_3	CH_3	10	8.83	17.2
1,1,1-Trifluoro-3,2'-furoylacetone	2-furyl	CF_3	11	8.5	17.2
Hexafluoroacetylacetone	CF_3	CF_3	12	6.0	

a) Measured in a dioxane (75%) - water solvent at 30°C by the glass electrode method. b) $CH_3COCH(CH_2)_4CO$. c) Estimated from Fig. 3.

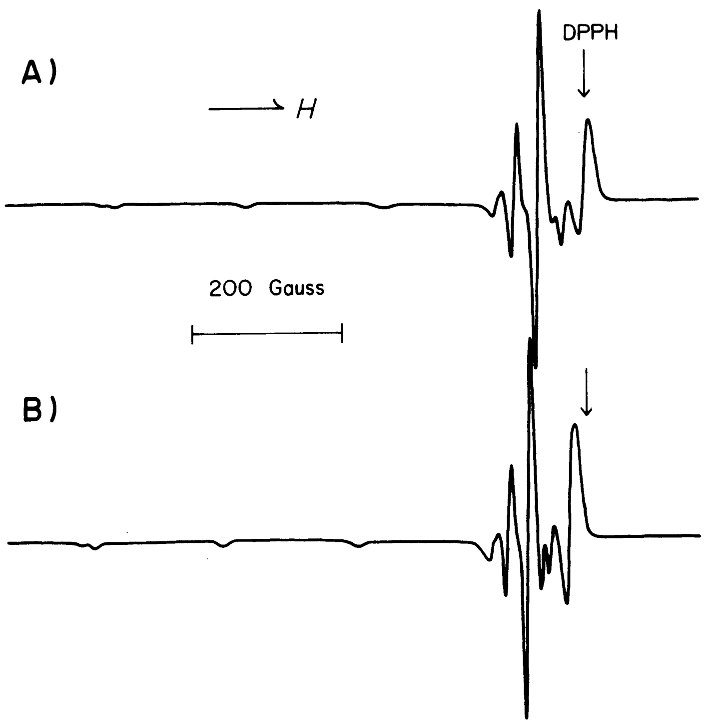


Fig. 1. ESR spectra in toluene (X-band, at 77°K).

a) Bis(dipivaloylmethanato)-copper(II),

b) Bis(1,1,1-trifluoroacetyl-acetonato)copper(II).

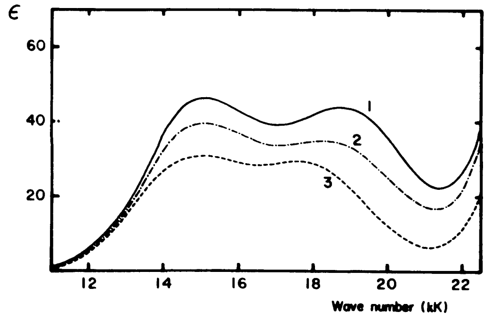


Fig. 2. Visible absorption spectra at room temperature in toluene.

1) Bis(dipivaloylmethanato)Cu(II),
2) Bis(acetylacetonato)Cu(II),
3) Bis(1,1,1-trifluoroacetylacetonato)Cu(II).

where λ(= − 828 cm^{-1}), ΔE_{xy}, and ΔE_{xz} have their usual meanings, and where $k_{/\!/}^2$ and $k_{\perp}^2$ are termed orbital reduction factors. The equations of $k_{/\!/}^2 \approx \alpha^2\beta_1^2$ and $k_{\perp}^2 \approx \alpha^2\beta^2$ hold good for square planar copper(II) complexes, where α, β_1, and β are the coefficients of the $d_{x^2-y^2}$, d_{xy}, and d_{xz},d_{yz} orbitals in the MO's to which they contribute. α^2, β_1^2, and β^2, consequently, measure the degrees of covalency of σ-bonding, in-plane π-bonding, and out-of-plane π-bonding respectively.

It is clear that there is little correlation between the pK_a and β_2 values listed in Table 1 in contrast to the well-known relationship between basic strength and stability first pointed out by Calvin.[4)] It was found in this study that all the experimentally-determined parameters have a linear relationship to the pK_a. The fact that the β_2 has little correlation with the other parameters for this series of complexes is considered to present some important problems in coordination chemistry, but it is difficult at present to discuss such problems deeply. Plots of $g_{/\!/}$ and $g_{\perp}$ against pK_a are shown in Fig. 3. This figure clearly indicates that both of $g_{/\!/}$ and $g_{\perp}$ linearly decrease with an increase of pK_a. The relationship between $g_{/\!/}$ and the hyperfine coupling constants, $A_{/\!/}$ and $A_{\perp}$, is shown in Fig. 4. A tendency for $|A_{/\!/}|$ to decrease uniformly with an increase of $g_{/\!/}$, which has been recognized for many other copper(II) complexes,[5)] is also in the present case, as shown in Fig. 4. Strictly speaking, the g and A tensors of the complexes under discussion were not of

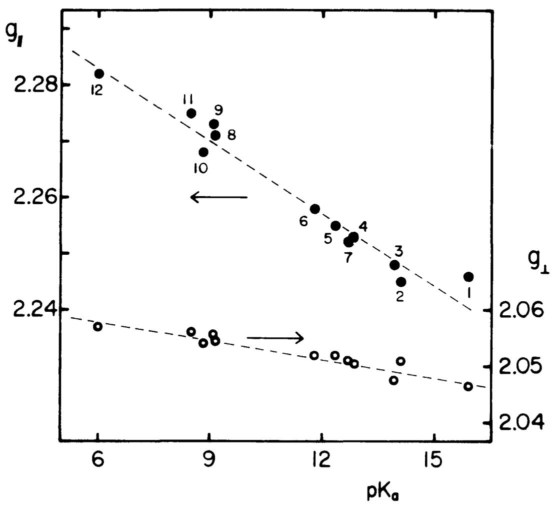


Fig. 3. Plots of $g_{/\!/}$ and $g_{\perp}$ against pK_a. Numbers correspond to the complexes listed in Table 1 (it is the same in other figures).

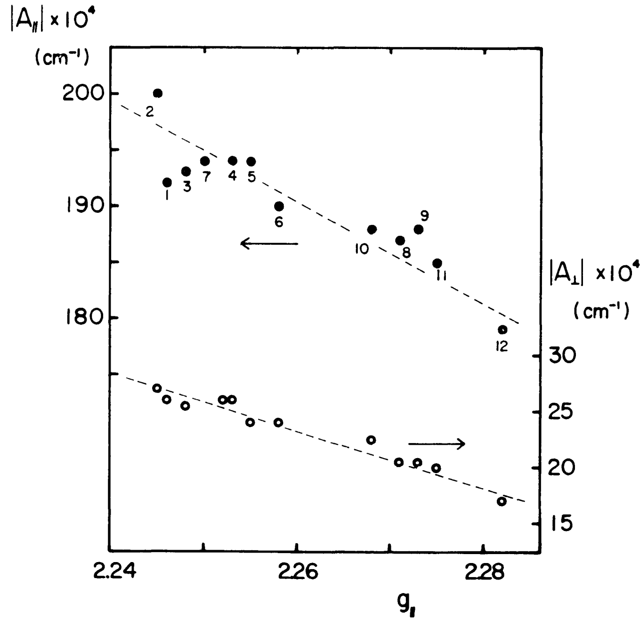


Fig. 4. Plots of $A_{\parallel}$ and $A_{\perp}$ against pK_a.

a completely axial symmetry, as can be seen in Fig. 1. The mean of the slightly different two vertical components, therefore, is expressed as $g_{\perp}$ and $A_{\perp}$ in Figs. 3 and 4 respectively.

The visible absorption data are shown in Fig. 5, where ΔE_1 and ΔE_2 are plotted against pK_a. Both of them turn out to increase slightly with pK_a. All the observed visible absorption spectra must consist of three d-d bands, on the assumption of D_{4h} symmetry. It is now necessary to estimate the energies of the three d-d bands as exactly as possible in order to evaluate the covalency parameters of coordination bondings from Eq. (1). Fortunately, a polarized spectral study of bis(benzoylacetonato)copper(II) in single crystals has been reported, and the results are as follows;[6] ΔE_{z^2} = 14.2 kK, ΔE_{xy} = 15.6 kK, and ΔE_{xz} = 18.1 kK. These results indicate that ΔE_2 is close to ΔE_{xz}, and that ΔE_1 is close to the mean of ΔE_{z^2} and ΔE_{xy} (ΔE_1 = 15.0 kK and ΔE_2 = 18.6 kK for this complex). Since toluene is a non-coordinating solvent, the band energies of the complexes in toluene do not differ largely from those in crystals. Accordingly, in this study the energy values of ΔE_{xz} and ΔE_{xy} were determined according to the assumptions of $\Delta E_2 = \Delta E_{xz}$ and $\Delta E_1 = (\Delta E_{z^2} + \Delta E_{xy})/2$ and, furthermore, to the assumption that the difference between ΔE_{z^2} and

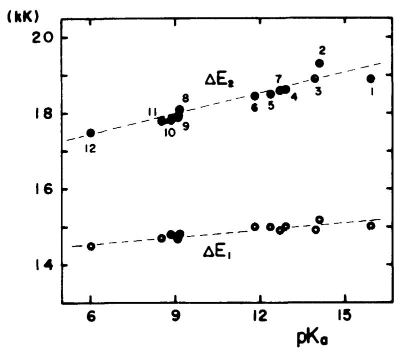


Fig. 5. Plots of ΔE_1 and ΔE_2 against pK_a.

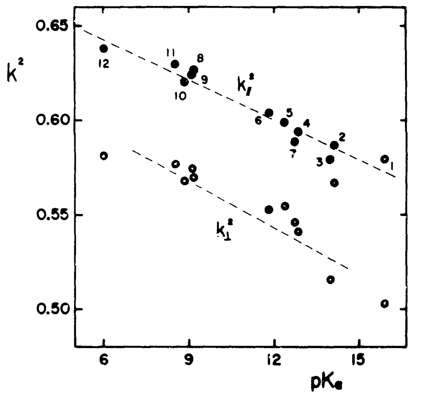


Fig. 6. Plots of $k_{/\!/}^2$ and $k_{\perp}^2$ against pK_a.

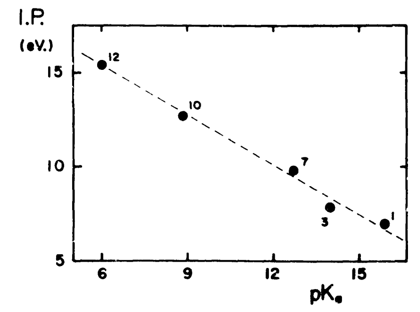


Fig. 7. A plot of the ionization potentials of the substituent radical, R•, against pK_a.

ΔE_{xy} is proportional to the one between ΔE_1 and ΔE_2.

The orbital reduction factors, which were calculated from Eq. (1) using all the data determined above, were plotted against pK_a; this is shown in Fig. 6. This figure indicates that both of $k_{/\!/}^2$ and $k_{\perp}^2$ decrease as pK_a increases, namely, that all the coordination bondings of σ-type, in-plane π-type, and out-of-plane π-type become more covalent as pK_a increases.

This result concerning the coordination bondings can be approximately explained in terms of the electron density at the oxygen atoms, since the mixing of the metal 3d orbitals and the ligand oxygen orbitals becomes large with a rise in the energy levels of the oxygen atomic orbitals caused by an increase of the electron density at the oxygen atoms.[7] The inductive effect of the α-substituents, R and R', must directly correlate with the electron density at the oxygen atoms. The ionization potentials of the substituent radicals may be taken as a measure of their inductive effects.[8] As Fig. 7 shows, there is a linear relationship between the ionization potentials and the pK_a values. Therefore, the pK_a values listed in Table 1 can be approximately regarded as a measure of the electron density at the oxygen atoms; the electron density increases uniformly as pK_a increases. This fact is in agreement with such a previously reported result that the pK_a of acids with π-electron conjugated systems has a linear relationship to the electron density at the protonated atoms calculated by means of Hückel M.O. method.[9]

Although both of protons and cupric ions are known to belong to Lewis acids, the results obtained here for this series of complexes indicate that not only the degree of covalency for the σ-bonding but also those for the π-bondings increase with pK_a. However, this information also does not give a clue to the explanation for the foregoing abnormality in the β_2. Further works on this point are now in progress.

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