Theoret. chim. Acta (Berl.) 3, 38—44 (1965)

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Interpretation of the Polarized Absorption Spectra of Single Crystals of Copper Acetylacetonate

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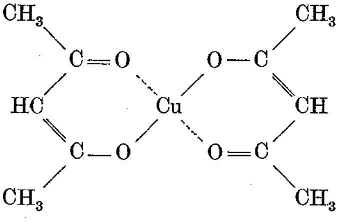
The electronic spectrum of a solution of the copper complex of acetylacetone as well as the spectra observed with polarized light of single crystals of the complex are reinvestigated. The observed bands are interpreted by the crystal-field theory.

Das Elektronenspektrum einer Lösung des Kupferkomplexes von Acetylaceton sowie die mit polarisiertem Licht beobachteten Spektren von Einkristallen des Komplexes werden einer erneuten Untersuchung unterzogen. Die beobachteten Banden werden an Hand der Kristallfeld-Theorie gedeutet.

Le spectre électronique du complexe de cuivre d'acétylacétone ainsi que les spectres — observés à l'aide de lumière polarisée — des cristaux uniques du complexe sont soumis à une nouvelle investigation. Les bandes trouvées sont interprétées suivant la théorie du champ cristallin.

Introduction

In the past attention was paid to the electronic structure of the copper complex of acetylacetone.



The polarized absorption spectra of single crystals of the complex were investigated by Ferguson [2]. The analysis of the spectra was recently extended by Piper and Belford [4]. These authors tried to explain the observed phenomena in terms of electronic processes occurring in the single molecules. Their results are not quite satisfactory, however. An assignment of the bands could not be given from the directions of the polarization observed. Therefore, a reinvestigation of the spectra of the copper complex of acetylacetone seemed desirable. We observed both the absorption spectrum of a solution of the complex molecule in chloroform and the absorption spectra obtained with polarized light of single crystals of the complex.

By an alternative description we interprete the observed phenomena as arising from electronic processes occurring in the whole crystal. The number of the absorption bands and the directions of the corresponding transition moments can be found by means of Davydov's crystal-field theory.

Symmetry of Molecule and Crystal

Piper and Belford state that in the gas phase the molecule will belong to the point group D_{2h}. According to Dahl's results [4] the symmetry appears to be slightly distorted in the crystal and a pseudo D_{2h} symmetry is adopted.

The copper complex of acetylacetone srystallizes in the monoclinic system. The space group is C_{2h}^5 ($P\,2_1/n$). There are two molecules per unit cell. The unit cell dimensions are

$$a = 11.40\ \text{Å}$$
$$b = 4.75\ \text{Å}$$
$$c = 10.33\ \text{Å} \qquad \beta = 92.2° \ .$$

Experimental

The copper complex of acetylacetone was prepared according to the procedure given by FERGUSON [*1*].

The spectrum of a solution of the substance in chloroform is represented in Fig. 1. The bands at 15,400, 18,350 and 26,300 cm^{-1} agree with those mentioned in the paper of PIPER and BELFORD [*4*]. In addition, two new absorption bands, at 32,700 and 33,700 cm^{-1}, were observed.

The spectrum of the copper complex of acetylacetone dissolved in chloroform was run on a Beckmann DK 2 spectrophotometer.

The single crystals were obtained by slow evaporation of the solvent of a solution of the complex of copper acetylacetonate in chloroform. The crystals were quite well developed, some tenths of a mm thick, and their (101) face predominated. The crystal spectrum was run on a Zeiss PMQ II spectrophotometer in conjunction with a Zeiss polarization microscope. The convergent incident light beam was perpendicular to the (101) face, with the plane of polarization parallel and perpendicular to the *b*-axis of the monoclinic crystal.

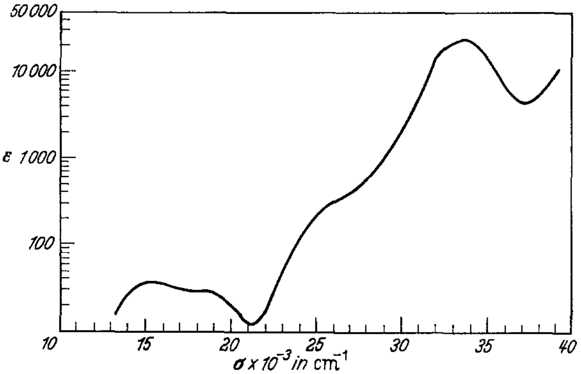


Fig. 1. Absorption spectrum of the copper complex of acetylacetone in chloroform

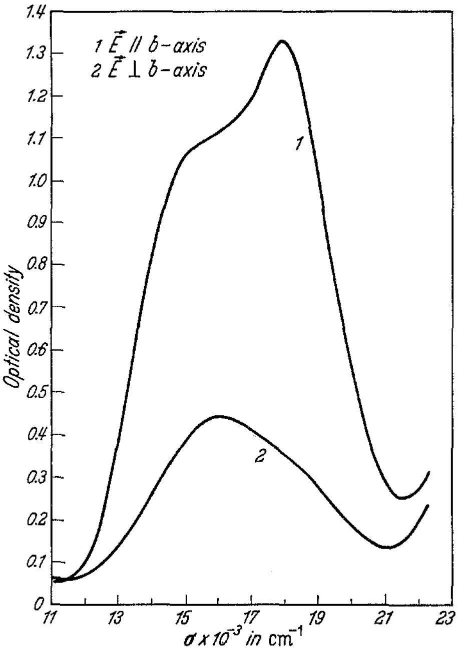


Fig. 2. Absorption spectrum of a single crystal of the copper complex of acetylacetone

The spectra are given in Fig. 2. Thefollowing transitions are observed:

about 15,600 cm^{-1} polarized parallel to the *b*-axis
16,100 cm^{-1} polarized perpendicular to the *b*-axis
18,000 cm^{-1} polarized parallel to the *b*-axis
about 18,500 cm^{-1} polarized perpendicular to the *b*-axis.

All measurements were carried out at room temperature.

Discussion

Recently Gray and Ballhausen [*3*] gave an extensive molecular orbital picture of the square planar metal complexes. Their considerations were restricted to molecules belonging to the point group D_{4h}. However, the conclusions can easily be extended to molecules of the point group D_{2h}. The resulting tentative molecular orbital energy diagram is given in Fig. 3.

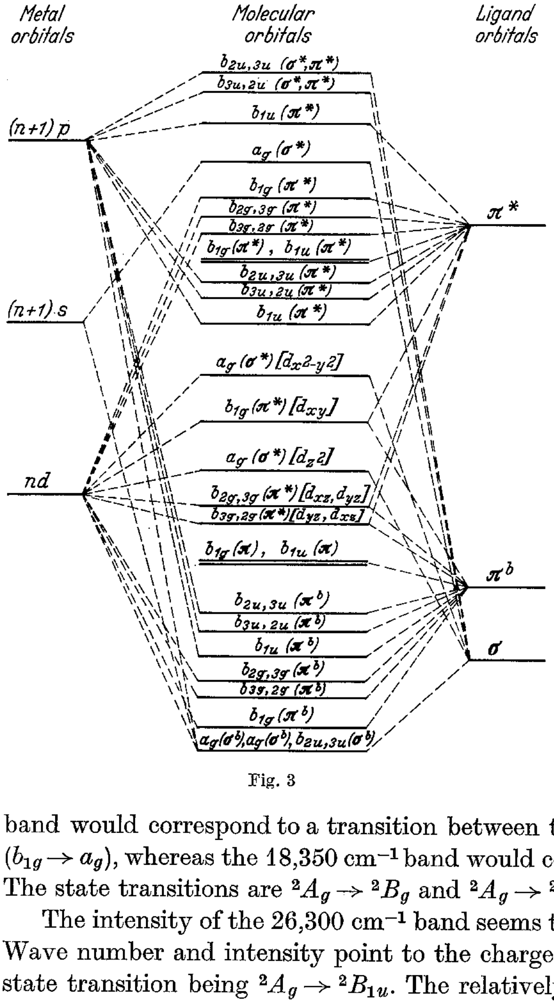


Fig. 3

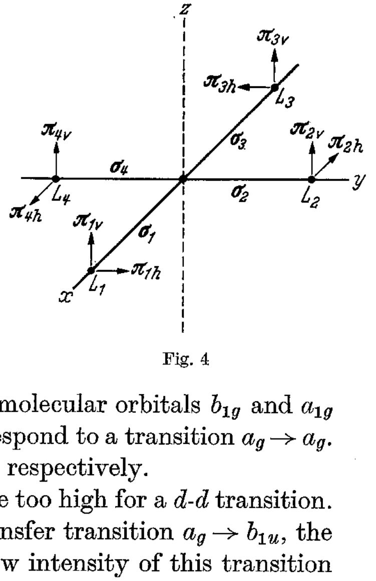


Fig. 4

Guided by the energy level diagram we may now interprete the spectrum of a solution of the complex as follows:

Both the wave numbers and the low intensities of the bands at 15,400 cm^{-1} and 18,350 cm^{-1} strongly suggest that these transitions correspond to *d*-*d* transitions. According to the energy level diagram the 15,400 cm^{-1} band would correspond to a transition between the molecular orbitals b_{1g} and a_{1g} ($b_{1g} \rightarrow a_g$), whereas the 18,350 cm^{-1} band would correspond to a transition $a_g \rightarrow a_g$. The state transitions are $^2A_g \rightarrow {}^2B_g$ and $^2A_g \rightarrow {}^2A_g$, respectively.

The intensity of the 26,300 cm^{-1} band seems to be too high for a *d*-*d* transition. Wave number and intensity point to the charge-transfer transition $a_g \rightarrow b_{1u}$, the state transition being $^2A_g \rightarrow {}^2B_{1u}$. The relatively low intensity of this transition comes up to expectation and may be understood from the following discussion.

The a_g molecular orbital is of the type

$$\varphi\,(a_g, \sigma^*) = c_M\, d_{x^2-y^2} + c_{L(\mathrm{I})} \left[\frac{1}{2}\,(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)\right] + c_{L(\mathrm{II})} \left[\frac{1}{2}\,(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)\right]$$

where the constants c_M and c_L are subject to group-theoretical and quantum-mechanical considerations. The wave functions are plotted in the co-ordinate system used by Gray and Ballhausen and are reproduced in Fig. 4.

The b_{1u} molecular orbital is given by

$$\varphi\,(b_{1u}, \pi^*) = c_M\,(n+1)\,p_z + c_L \left[\frac{1}{2}\,(\pi_{1v} + \pi_{2v} + \pi_{3v} + \pi_{4v})\right].$$

The transition moment of the charge-transfer transition $a_g \rightarrow b_{1u}$ will be

$$\langle \varphi\,(a_g, \pi^*)\,|\,e\vec{r}\,|\,\varphi\,(b_{1u}, \pi^*)\rangle\ .$$

As the $d_{x^2-y^2}$-orbital is mainly concentrated in the (x, y) plane and the p_z-orbital points along the z-axis, the magnitude of the transition moment will be small and a rather low intensity can be expected. This is what is actually observed.

The wave numbers and the intensities of the transitions at 32,700 cm^{-1} and 33,700 cm^{-1} point strongly to the transitions $a_g \rightarrow b_{2u,\,3u}$ and $a_g \rightarrow b_{3u,\,2u}$, corresponding to allowed charge-transfer transitions. The wave function $\varphi\,(b_{2u,3u}, \pi^*)$ is given by

$$\varphi(b_{2u,\,3u}, \pi^*) = c_M\,(n+1)\,p_x + c_{L(\mathrm{I})}\left[2^{-\frac{1}{2}}\,(\pi_{2h} - \pi_{4h})\right] + c_{L(\mathrm{II})}\left[2^{-\frac{1}{2}}\,(\pi_{1h} - \pi_{3h})\right]$$

and the wave function $\varphi\,(b_{3u,\,2u}, \pi^*)$ is represented by

$$\varphi\,(b_{3u,\,2u}, \pi^*) = c_M\,(n+1)\,p_y + c_{L(\mathrm{I})}\left[2^{-\frac{1}{2}}\,(\pi_{2h} - \pi_{4h})\right] + c_{L(\mathrm{II})}\left[2^{-\frac{1}{2}}\,(\pi_{1h} - \pi_{3h})\right].$$

A consideration – analogous to that given above – of the transition moments reveals that both the transition moments would be large and equal. In the experiment a small difference in intensity has been observed. This may be caused by the fact that the O-Cu-O angle deviates from 90°. The results of the discussion given above are summarized in the table.

Table

Wave number	Intensity	State Transition	Molecular Orbital Transition	
15,400 cm^{-1}	$\varepsilon \approx 30$	${}^2A_g \rightarrow {}^2B_g$	$b_{1g} \rightarrow a_g$	orbitally forbidden
18,350 cm^{-1}	$\varepsilon \approx 30$	${}^2A_g \rightarrow {}^2A_g$	$a_g \rightarrow a_g$	orbitally forbidden
26,300 cm^{-1}	$\varepsilon \approx 300$	${}^2A_g \rightarrow {}^2B_{1u}$	$a_g \rightarrow b_{1u}$	allowed
32,700 cm^{-1}	$\varepsilon \approx 20{,}000$	${}^2A_g \rightarrow {}^2B_{2u,\,3u}$	$a_g \rightarrow b_{2u,\,3u}$	allowed
33,700 cm^{-1}	$\varepsilon \approx 20{,}000$	${}^2A_g \rightarrow {}^2B_{3u,\,2u}$	$a_g \rightarrow b_{3u,\,2u}$	allowed

As is well known, the *d-d* transitions are orbitally forbidden. The transitions may arise, however, if some ungerade electronic wave function is mixed in owing to vibronic coupling.

Suppose q represents a vibrational co-ordinate of symmetry Γ_q. Expanding the crystalline field potential V in the vibrational co-ordinates gives

$$V = V_0 + \sum_i q_i \left(\frac{\partial V}{\partial q_i}\right)_0 + \ldots$$

V transforms as the trivial representation of the point group under discussion. Consequently, the same will hold for the product

$$q_i \left(\frac{\partial V}{\partial q_i}\right)_0 .$$

Suppose that the wave function representing the ground state transforms as Γ_0, and the wave function of the excited state to which the transition occurs transforms as Γ_1.

By first-order perturbation theory we can mix some higher excited states into the excited state Γ_1.

$$\varphi'(\Gamma_1) = \varphi(\Gamma_1) - \frac{q(\Gamma_q)\langle\varphi(\Gamma_1)\,|\left(\frac{\partial V}{\partial q_i}\right)_0|\,\varphi(\Gamma_i)\rangle}{E(\Gamma_1)-E(\Gamma_i)}\,\varphi(\Gamma_i)\ .$$

It will be clear that the direct product $\Gamma_1 \times \Gamma_q \times \Gamma_i$ must transform as the trivial representation in order that the first-order perturbation will be non-vanishing.

The transition $\Gamma_0 \rightarrow \Gamma_1$ is now partially allowed and the intensity can be borrowed from the intensity of the transition $\Gamma_0 \rightarrow \Gamma_i$.

A condition to be fulfilled is that

$$\Gamma_0 \times \Gamma_r \times \Gamma_i$$

contains the trivial representation of the point group under consideration. Summarizing, we may state that two conditions must be fulfilled

$$\Gamma_1 \times \Gamma_q \times \Gamma_i = A_{1g}$$

and

$$\Gamma_0 \times \Gamma_r \times \Gamma_i = A_{1g}\ .$$

Note that the conclusion in the paper of PIPER and BELFORD [4], viz.

$$\Gamma_0 \times \Gamma_q \times \Gamma_r \times \Gamma_1 = A_{1g}$$

is a necessary, but not a sufficient condition. Their conclusions are, consequently, not right in some respects. Only the α_u ungerade vibration is active.

The interpretation of the polarized absorption spectrum of the crystal of the copper complex of acetylacetone will be given in terms of DAVYDOV's crystal-field theory.

The ground state of the single molecule is assumed to have A_g symmetry, whereas the first excited state possesses B_{1g} symmetry. The transition ${}^2A_g \rightarrow {}^2B_{1g}$ is forbidden.

Owing to vibronic interaction, the wave function representing the excited state becomes

$$\varphi'(B_{1g}) = \varphi(B_{1g}) - \alpha\,\varphi(B_{1u}) - \beta\,\varphi(B_{2u}) - \gamma\,\varphi(B_{3u})\ .$$

In the single molecule the transition ${}^2A_g \rightarrow {}^2B_{1g}$ now becomes allowed. It seems reasonable, however, to neglect the contribution of $\varphi(B_{1u})$, as the transition ${}^2A_{1g} \rightarrow {}^2B_{1u}$ has a rather low intensity.

The ground state of the crystal will be given by

$$\Phi_0 = \prod_{n\alpha} \varphi^0_{n\alpha}(A_g) \qquad n = 1, \ldots N\ ; \qquad \alpha = 1, \ldots \sigma\ .$$

N denotes the number of unit cells in the crystal, while σ corresponds to the number of molecules in the unit cell.

If a molecule, $n\alpha$, is excited by absorption of dipole radiation, the following wave function arises

$$\Psi^f_{n\alpha} = \varphi^f_{n\alpha}(B_{1g}) \prod_{m\beta \neq n\alpha} \varphi^0_{m\beta}(A_g)\ .$$

Taking into account the exchange permutation, we obtain

$$\chi^f_{n\alpha} = [(S\sigma N)!]^{-\frac{1}{2}} \sum_P (-1)^P\, P\, \Psi^f_{n\alpha}$$

(S is the number of participating electrons per molecule.)

The resulting wave function of the excited state of the crystal will be

$$\Phi f = (\sigma N)^{-\frac{1}{2}} \sum_{n\alpha} a_{n\alpha} \chi^f_{n\alpha} .$$

For two molecules per unit cell

$$\Phi^f_1 = (2N)^{-\frac{1}{2}} \sum_{n} (\chi^f_{n1} + \chi^f_{n2})$$

$$\Phi^f_2 = (2N)^{-\frac{1}{2}} \sum_{n} (\chi^f_{n1} - \chi^f_{n2}) .$$

Now the ground state will have A_g symmetry, whereas $\chi^f_{n\alpha}$ will transform under B_{1g}. As a consequence

$$\Phi^{(B_{1g})'}_1 = (2N)^{-\frac{1}{2}} \sum_{n} (\chi^{(B_{1g})'}_{n1} + \chi^{(B_{1g})'}_{n2})$$

$$\Phi^{(B_{1g})'}_2 = (2N)^{-\frac{1}{2}} \sum_{n} (\chi^{(B_{1g})'}_{n1} - \chi^{(B_{1g})'}_{n2}) .$$

It turns out to be that

$$\Phi^{(B_{1g})'}_1 \in B_u$$

and

$$\Phi^{(B_{1g})'}_2 \in A_u .$$

As a consequence, two transitions can be expected:

1. $A_g \rightarrow B_u$ polarized perpendicular to the b-axis,
2. $A_g \rightarrow A_u$ polarized parallel to the b-axis.

The absorption band observed at 15,400 cm^{-1} in a solution of the copper complex of acetylacetone will split into two transitions. This is actually observed in the crystal. The transitions are at 15,600 and 16,100 cm^{-1}, respectively.

The next excited state of the single molecule has A_g symmetry. The vibronic interaction mechanism causes a slight mixing with the wave functions representing the states B_{1u}, B_{2u} and B_{3u}.

$$\varphi' (A_g) = \varphi (A_g) - \alpha \varphi (B_{1u}) - \beta \varphi (B_{2u}) - \gamma \varphi (B_{3u}) .$$

The transition $A_g \rightarrow A_g$ now becomes allowed.

Again, the ground state of the crystal is represented by the wave function

$$\Phi_0 = \prod_{\sigma N} \varphi^0_{n\alpha} (A_g) .$$

However, the excited state will be represented by

$$\Psi^f_{n\alpha} = \varphi^f_{n\alpha} (A_g) \prod_{m\beta \neq n\alpha} \varphi^0_{m\beta} (A_g) .$$

Proceeding in the same way as above, we obtain

$$\Phi^{(A_g)'}_1 = (2N)^{-\frac{1}{2}} \sum_{n} (\chi^{(A_g)'}_{n1} + \chi^{(A_g)'}_{n2})$$

$$\Phi^{(A_g)'}_2 = (2N)^{-\frac{1}{2}} \sum_{n} (\chi^{(A_g)'}_{n1} - \chi^{(A_g)'}_{n2}) .$$

It turns out that

$$\Phi_1^{(A_g)'} \in B_u$$
$$\Phi_2^{(A_g)'} \in A_u \ .$$

As a consequence, two transitions can be expected:

1. $A_g \rightarrow B_u$ polarized perpendicular to the b-axis,
2. $A_g \rightarrow A_u$ polarized parallel to the b-axis.

The absorption band observed at 18,350 cm^{-1} in a solution of the copper complex of acetylacetone will split into two transitions. In the crystal measurements these transitions are found at 18,000 and 18,500 cm^{-1}, respectively.

Concluding, we state that the crystal spectra can be interpreted in a satisfactory way by Davydov's crystal-field theory. The theory gives the right number of the bands observed and the predicted directions of the transition moments agree with the observed data. The magnitude of the energy split is difficult to predict, but the order of magnitude comes up to expectation.

Acknowledgements. I wish to thank Dr. C. Bokhoven for his stimulating remarks, Dr. A. Dijkstra for his helpful crystallographic discussions and Mr. J. P. G. Rousseau, Mr. T. B. Katinger and Mr. J. P. C. van Heel for their experimental assistance. I owe Professor M. P. Groenewege for critically reading the manuscript.

Note added in proof: After submitting the paper to Theoretica Chimica Acta we extended the crystal measurements to the temperature of liquid nitrogen. At 77° K the spectrum shows all the bands mentioned above, resolved. There appears to be a blue shift of the bandsystem at liquid nitrogen temperature of about 250 cm^{-1}, whereas the intensity of the bands shows some decrease.

Literature

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(Received November 10, 1964)