Study on the Molecular Structure of Bisacetylacetone-Copper(II) by Electron Diffraction[1]

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Although the structures and properties of metallic chelate compounds have attracted considerable attention of many recent investigators, the number of compounds whose molecular structures have been accurately determined by X-rays seems to be rather limited on account of their highly complicated crystal structures. However, it is well known that some of these compounds can readily be vaporized. Therefore, it is possible to apply the gas electron diffraction method to the determination of their molecular structures. The present paper deals with the study on the molecular structure of copper chelate of acetylacetone by this method.

The structure of copper acetylacetonate is of interest, particularly, in respect to the question whether the configuration of four oxygen atoms relative to the divalent copper atom is square or tetrahedral, from the point of view of the metallic chelate chemistry. Such a problem has not yet been completely clarified in spite of many earlier investigations, e.g. X-ray analysis[2], dipole moment[3] and infra-red absorption[4] measurements. Our present electron diffraction study was intended to obtain such information, and directly clarified the fact that the chelate possesses a square planar configuration with

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[1] Presented at Symposium on the metallic complex compounds held on November 13, 1951.

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[2] E. G. Cox and K. C. Webster, *J. Chem. Soc.*, 1935, 731.

[3] A. E. Finn, G. C. Hampson, and L. E. Sutton, *J. Chem. Soc.*, 1938, 1254.

[4] e.g. J. Lecomte, *Discussions Faraday Soc.*, 1950, 125.

Cu-O distance equal to 1.95 Å. Our results were in good agreement with the recent X-ray investigations[5,6].

Experimental

The sample was prepared by the reaction of aqueous cupric acetate solution with acetylacetone. It was recrystallized from alcohol. The sample was evaporated at about 170°C in a high temperature nozzle and was led into a vacuum chamber to interfere with an electron beam of about 0.06 Å in wave length. The diffraction photographs were taken in the usual way[7]. The camera length was about 11 cm.

Analysis

Measurements were made visually of the q values and the intensities of maxima and minima below $q=70$ in the photographs. Only the intensity of the 14th maximum could be measured. The measured q values are listed in Table I.

TABLE I

OBSERVED AND CALCULATED q VALUES OF THE MAXIMA AND MINIMA

Max.	Min.	$q_{\text{obs.}}$	q_c(Model C)	$q_c/q_{\text{obs.}}$[a]
	2	7.56	7.6	(1.005)
2		10.05	10.2	1.015
3		14.61	14.7	1.006
4		17.82	17.4	(0.976)
5		21.05	21.0	0.998
6		24.83	23.6	(0.950)
7		29.18	29.6	1.014
8		33.71	33.5	0.994*
9		37.85	36.9	(0.975)
10		43.32	43.3	1.000*
11		52.06	52.2	1.003*
12		57.29	56.4	0.984
13		62.77	62.0	0.988
Average of $q_c/q_{\text{obs.}}$				1.000
Average Deviation				0.007

a) The values in parentheses were omitted in calculating the average and values marked with asterisk were given double weight.

The positions of the minima except the 2nd were not measured because of the highly short period of the halos. Curve V_1 in Fig. 3 shows the visual curve which was drawn so as to reproduce the feature of halos and to have the intensities corresponding to the following formula.

$$I(q)=\sum_{i\neq j}(Z_iZ_j/r_{ij})\sin(\pi qr_{ij}/10)$$

Here notations have their usual significances. However, the accurate measurement of intensity in the region of small q values is considerably difficult on account of the intense background of photographs; hence it is probable that the inaccuracy of intensity measurement introduces errors into the radial distribution curve. Therefore the intensity of the first visual curve in this region was corrected by the preliminary theoretical intensity curves in a way described below. The R.D. curve was calculated from the visual curve by use of the formula

$$rD(r)=\sum_i I(q_i)\exp(-aq_i^2)\sin(\pi q_i r/10),$$

where the constant a was chosen so that $\exp(-aq_i^2)=0.1$ for the last term ($q_i=65$). In this case, the unobservable part of q below 7 which is shown by a dotted curve in V_1 in Fig. 3 was appropriately estimated from the feature of the theoretical intensity curve. The R.D. curve thus obtained is shown by R.D. 1 in Fig. 1. The interatomic distances obtained from this curve are given in Table 2 with assignments to these distances. It must be mentioned here that the following assumption was made throughout the present analysis; the ligand is planar and possesses D_{2h} symmetry. Using the values obtained for the interatomic distances, especially, Cu-O$_1$**, Cu-C$_1$, Cu-C$_2$, and Cu-C$_4$, preliminary theoretical intensity curves were calculated for various reasonable models. Then, it can be seen that these models*** did not seriously change the

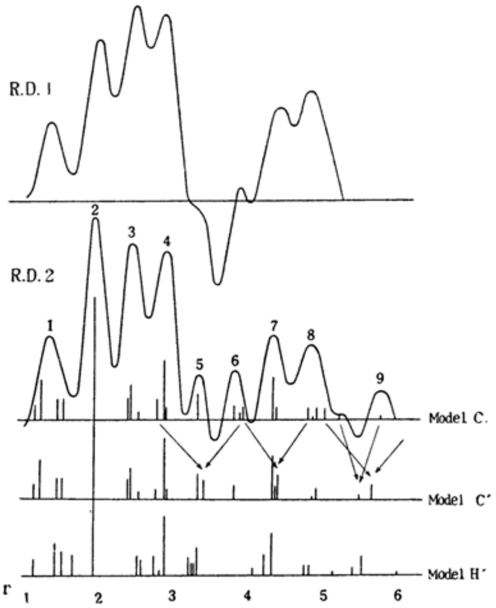

Fig. 1. The radial distribution curves of copper acetylacetonate.

The vertical bars in R.D. 2 indicate all atomic distances (below 6 Å) calculated for model C (square planar), model C′ (rectangular twisted) and model H′ (tetrahedral).

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[5] E. A. Shugam, *Doklady Akad. Nauk S.S.S.R.* **81**, 853 (1951); *Chem. Abst.*, **46**, 3894 (1952).

[6] H. Koyama, Y. Saito and H. Kuroya, *Journal of the Institute of Polytechnics, Osaka City University*, **4**, No. 1, Series C., 43 (1953).

[7] e.g. L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

** The notation "Cu-O$_1$" also means Cu-O$_1$', Cu-O$_2$ and Cu-O$_2$'. In the case of other atomic pairs the situation is the same as in the Cu-O$_1$ by the above assumption.

*** A twisted model is also taken into consideration together with a planar model.

TABLE II

THE POSITIONS AND THE ASSIGNMENTS OF THE PEAKS IN THE R.D. CURVES

Peak	Distance Å		Assignment[a)]
	R.D. 1	R.D. 2	
1	1.34	1.34	$C_1O_1(3)$ $C_1C_2(2)$ $C_1C_4(2)$ CH(1)
2	1.97	1.95	$CuO_1(10)$
3	2.44	2.41	$C_2O_1(2)$ $C_4O_1(2)$ $C_2C_4(1)$
4	2.84	2.87	$CuC_1(5)$ O_1O_2, $O_1O_{2'}$*(2) $O_1C_3(1)$
5	3.25	3.32	$CuC_2(2)$
6	3.82	3.80	C_1C_5*(1) $O_1C_{3'}(1)$
7	4.32	4.30	$CuC_4(3)$ $O_1C_5(1)$
8	4.80	4.81	$O_1C_{1'}$*(1) $O_1C_{2'}(1)$ $O_1C_{5'}(1)$
9		5.72	$C_1C_{1'}$

a) These assignments correspond to the most probable model C. Numbers in parentheses show approximately the relative magnitudes of the ratio Z_iZ_j/r_{ij}. Here the atomic pairs contributing predominantly to each peak are listed. Also the italicized atomic distances are assumed in the calculation of the intensity curves. The bond distances marked with asterisks vary depending on the configuration of the molecule.

intensities for small q values, and therefore the features of these curves can be used to modify the intensity of the first visual curve for small q values (below about 15). The visual curve thus corrected is shown by V_2 in Fig. 3. For example, it was found that the height of the 2nd maximum and the depths of the 2nd and 3rd minima were overestimated in the first visual curve.

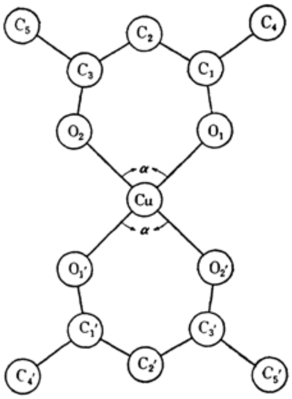

Fig. 2. The shape of the best model and the numbering of atoms.

The corrected R.D. curve was further calculated from the second visual curve in the same way as before, and is shown by R.D. 2 in Fig. 1. This curve is almost non-negative, and this fact is a desirable feature in general. Table II lists the positions and assignments of peaks in its curve. The 2nd, 4th, 5th and 7th peaks are definitely assigned to the $Cu-O_1$, $Cu-C_1$, $Cu-C_2$ and $Cu-C_4$ atomic pairs, respectively, since these peaks are taken as single or nearly single peaks because of their great scattering powers, so these distances seem to be probably correct. If the structures of the ligands are assumed as mentioned above, the geometrical consideration of the 3rd peak (assigned to C_2-O_1, C_4-O_1 and C_2-C_4) with the above four distances leads to the value of $\angle O_1CuO_2(\angle\alpha)$ nearly equal to 90°. Furthermore, the complete structure of the ligand is probably estimated with use of the 6th peak (C_1-C_5); thus the structure of ligand of the square model C is selected as the most probable model. Thus the structure of the molecule is determined by the configuration dependent on the angle between two ligand planes. Therefore, to determine particularly whether the configuration of molecule is coplanar (model C) or rectangular (model C′), computed radial distributions for each model were compared with the observed one. The vertical bars under the R.D. 2 in Fig. 1 show the interatomic distances for each model and the heights of the bars are drawn proportional to Z_iZ_j/r_{ij} of the respective atomic pairs. Oblique arrows in this figure show the corresponding atomic pairs by the change of the molecular configuration. The comparison of the two computed radial distributions with the observed one leads to the fact that the planar model is superior to the rectangular twisted model, because in the latter the areas of the 5th, 6th, 7th and 8th peaks are not in quantitative accordance with the sum of the heights of the bars. This fact will be made clear by the comparison of both theoretical intensity curves with the observed curve as described later.

Furthermore, a large number of theoretical intensity curves were calculated for various molecular models in order to check the acceptability of the most probable model C mentioned above and to determine the molecular structure in more detail. However, on account of the many parameters involved a complete analysis on the molecular structure of copper acetylacetonate would be a very laborious task. Therefore this analysis was carried out by means of the following assumptions: $Cu-O_1$, $Cu-C_1$, $Cu-C_2$, and $Cu-C_4$ distances are 1.95 Å, 2.87 Å, 3.32 Å and 4.30 Å, respectively, which are the most probable values obtained from R.D. method. Then other parameters determining the structure are $\angle\alpha$, C_1-C_2, and C_1-C_4 for the ligands, and the configuration of the molecule dependent on the angle between the two ligand planes. The values of the parameters $\angle\alpha$ and C_1-C_2 were taken over the range from 80° to 110° and from 1.33 Å to 1.62 Å respectively, and the position of the C_4 atom was taken in such a way that the C_1-C_4 bond nearly bisects $\angle O_1C_1C_2$. In regard to the configuration of molecule, a coplanar and a rectangular form (including a tetrahedral form) are taken into account. A number of intensity curves were calculated for these carefully selected models with various values for the above parameters and were compared with the observed one. These intensity curves contain the contributions from all the atomic pairs, the pairs pertaining to hydrogen being ignored except H–C bondings.

Some of the calculated intensity curves are depicted in Fig. 3. The corresponding models are listed in Table III. The relative positions and features of maxima and minima of these curves will be compared with those of the visual curve as follows. Curve A is unsatisfactory since the 8th maximum is low and since the 10th minimum is shallow, and since the 11th maximum is lower than the 12th maximum. If the value of $\angle\alpha$ is smaller than 80°, the intensity curves cannot be obtained in agreement with the observed one in regard to the points mentioned above, even though various values of other parameters**** were used. Therefore model A provides the lower limit of $\angle\alpha$. Curves B and E are satisfactory. Curves C and D are more satisfactory. Curve F is unsatisfactory because of the feature of the 9th maximum (depressed to an unacceptable extent) and the relative heights and the positions of the 11th and 12th maxima, and this model provides the upper limit of $\angle\alpha$. Model H*****, a planar model with $\angle\alpha$ equal to a tetrahedral angle, is very unsatisfactory because it requires that the heights of the 3rd and 6th maxima and especially the features of the 7th, 8th and 9th maxima disagree with observations. If the molecule takes a configuration with one ligand plane at a right angle to the plane of the other ligand, such as in models C′, E′, G′ and H′ (the latter two are tetrahadral), the features of the 3rd and 4th (disappearing) maxima and position of 5th maximum disagree remarkably with those of the visual curve as seen in Fig. 3, so that these twisted models (including the tetrahedral) are rejected. This conclusion was also confirmed by the computed R.D. as shown by C′ and H′ (tetrahedral) in Fig. 1. If the molecule would take the twisted form, the 5th and 7th peaks in the observed R.D. should be larger and the 6th and 8th peaks should be smaller. After all, the general qualitative appearance of the photographs is well reproduced by the square planar model. A quantitative comparison of the q values of maxima calculated for the best model C with the observed one is shown in Table I. The discrepancies in the positions of the 4th, 6th and 9th are presumably due to errors in the measurement, errors of this type being rather common. Also it must be mentioned that although the effect of molecular vibration was taken into account, it did not seriously affect the positions and the features of maxima and minima for q value below 65.

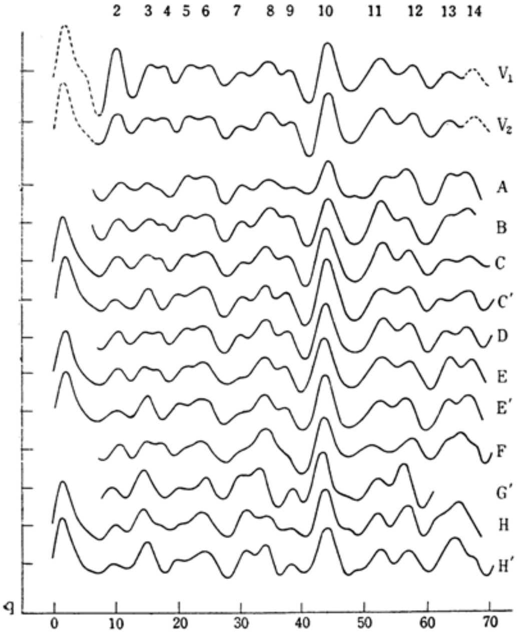

Fig. 3. Visual and theoretical intensity curves.

TABLE III

THE MODELS OF THE THEORETICAL INTENSITY CURVES SHOWN IN FIG. 3

Model	∠OCuO	C_1-C_2, Å	C_1-O_1, Å	C_1-C_4, Å	Configuration*
A	80°	1.33	1.15	1.55	Coplanar
B	90°	1.33	1.28	1.55	,, (Square form)
C	90°	1.46	1.21	1.51	,, (,,)
C′	,,	,,	,,	,,	Rectangular
D	90°	1.46	1.21	1.56	Coplanar (Square form)
E	93°	1.46	1.25	1.56	,,
E′	,,	,,	,,	,,	Rectangular
F	98°	1.45	1.32	1 51	Coplanar
G′	110°	1.46	1.50	1.51	Rectangular (Nearly tetrahedral form)
H	110°	1.62	1.40	1.50	Coplanar
H′	,,	,,	,,	,,	Rectangular (Nearly tetrahedral form)

* The configuration is determined by the twisted angle between two ligand planes.

From the analysis described above, the molecular structure of copper acetylacetonate was

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**** In general the feature of intensity curves are not seriously sensitive to the parameters C_1-C_2 and C_1-C_4.

***** The models with $\angle\alpha$ equal to a tetrahedral angle seems to be unresonable since the ligand require unreasonably long C_1-C_2 or C_1-O_1 distances from the previous assumption.

determined as follows: Cu–O$_1$=1.95 Å, Cu–C$_1$=2.87 Å, Cu–C$_2$=3.32 Å and Cu–C$_4$=4.30 Å, (These values were obtained from the R.D. method and the correctness of these values were checked by the calculations of the theoretical intensity curves.), $\angle O_1CuO_2 = 90 \pm 10^\circ$, and planar configuration. The latter two are more important conclusions. On the basis of the present photographs it is not possible to make any definite statements as to the distances of C$_1$–C$_2$, C$_1$–O$_1$ and C$_1$–C$_4$ on account of the complexity of the chelate, but for these distances the following average values are obtained from the acceptable models: 1.42 Å, 1.25 Å and 1.55 Å, respectively.

Discussion

Our gas electron diffraction study lead to the conclusion that copper acetylacetonate has a square coplanar configuration with Cu–O distance equal to 1.95 Å.

The result that this chelate takes a square coplanar configuration agrees with the earlier indication of Cox and Webster[2] and also with the recent data of Shugam[5] and Koyama et al.[5] (The $\angle O_1CuO_2$ was determined to be 93° by Shugam and 87.5° by Koyama et al., respectively.) The fact that the chelate forms the square coplanar (not tetrahedral) configuration seems to be due to the fact that an unpaired electron in the 3d orbital of Cu (II) is promoted to the 4p orbital so that Cu (II) constructs dsp^2 hybrid orbitals which have higher bond strengths than sp^3 hybrid orbitals, as suggested by Pauling[8]. Also in this case the conjugation between dπ orbital of Cu atom and pπ orbitals of the ligand atoms may highly strengthen the Cu–O bonds, so that this configuration will become more stable.

The observed value of the Cu–O distance was 1.95 Å. It is in good agreement with the sum of the covalent radius of oxygen (0.66 Å) and the metallic radius[8] of copper with a coordination number of 12 (1.28 Å), but is much smaller than the sum (2.4 Å) of ionic radii****** of the two atoms. This supports the evidence of covalent bond character of Cu–O bond. The Cu–O distances in various molecules hitherto reported are: 1.95 Å for cupric oxide[9], 2.01 Å for CuCl$_2$·2H$_2$O[9], 1.97 Å for K$_2$CuCl$_4$·2H$_2$O and (NH$_4$)$_2$CuCl$_4$·2H$_2$O[9], 1.98 Å and 2.01 Å (mean values) for two types of Cu atoms of malachite[10], 1.98 Å for bandylite[11], 2.03 Å for copper proline dihydrate[12], and 1.91 Å and 1.96 Å (mean values) for copper acetylacetonate (by Shugam and Koyama et al., respectively). The observed Cu–O distance agrees fairly well with these values, but better with that of cupric oxide than with others. This seems to be due probably to the fact that in cupric oxide Cu (II) takes a square coplanar configuration with four covalent Cu–O bonds as in a free molecule of copper acetylacetonate, rather than a distorted octahedral configuration as found in other examples mentioned above. Consequently the observed Cu–O distance of 1.95 Å corresponds to the covalent radius 1.29 Å for Cu (II) in square configuration with coordination number of 4, in contrast with the known radius[8], 1.35 Å in tetrahedral configuration.

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****** Pauling's univalent ionic radii were used after the correction for the ionic valence and coordination number.

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