Studies on the Molecular Structure of Bisacetylacetone-Nickel(II) by Electron Diffraction[*,1)]

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Recently, the structures and the properties of metal chelate compounds have attracted considerable attention of many investigators. Acetylacetone chelate is a repesentative of such metal chelate compounds. The author has already investigated the structure of bisacetylacetone-copper(II)[2)]. The present paper deals with the structure of bisacetylacetone-nickel(II).

It is interesting to decide whether the arrangement of four oxygen atoms of bisacetylacetone-nickel(II) about the bivalent nickel atom is planar or tetrahedral. The structure of this chelate has already been investigated by magnetic measurements[3)] and by absorption spectra[4)]. On the basis of the paramagnetic property of bisacetylacetone-nickel(II), Pauling[5)] presumed that the chelate has a tetrahedral configuration. However, this evidence has not yet been clarified by other more powerful methods, e.g., the preparation of isomers and the X-ray investigation. In particular, the latter is the most direct method to determine the molecular structure. Recently, the X-ray analysis has been taken by Bullen[6)], who showed that there are three nickel atoms in an asymmetric unit, the three atoms being very nearly collinear. Unfortunately he could not definitely clarify the molecular structure of the chelate. The acetylacetone chelate can readily be vaporized without suffering decomposition at a high temperature. Therefore the author has undertaken to apply the electron diffraction method to determine the molecular structure of the nickel chelate in the same way as in a previous study on the copper chelate.

Experimental

Bisacetylacetone-nickel(II) recrystallized several times from ethanol was furnished by Dr. K. Sone. The anhydrous compound was prepared by sublimation in vacuo. The apparatus[7)] used was that already reported by the present author and his collaborators. The sample was vaporized at about 170°C and led through a high temperature nozzle into a vacuum chamber to interfere with an electron beam of about 0.06 Å in wavelength. Non-sector photographs (The camera length was about 11 cm.) were taken in the usual way. Further examination was carried out by r^2 sector photographs (The camera length was about 12 or 28 cm.)

Visual Curve and Radial Distribution Curve

Visual measurements were made of the q values and the intensities of maxima

TABLE I

THE OBSERVED AND THE CALCULATED q VALUES OF THE MAXIMA AND THE MINIMA.

max.	min.	$q_{\text{obs.}}$	$q_{\text{calc.}}$ (model F)	$q_{\text{calc.}}/q_{\text{obs.}}$ a)
	2	7.66	7.7	(1.005)
2		10.20	10.2	1.000
3		14.92	15.0	1.005
4		17.85	17.5	0.980
5		21.26	21.2	0.997
6		24.10	23.7	0.992
7		28.73	29.2	1.016
8		34.40	34.3	0.997*
	10	40.78	40.4	0.991
10		44.07	43.9	0.996*
	11	48.28	48.3	1.000
11		51.44	52.4	1.019
12		58.22	57.6	0.990
13		65.62	65.6	1.000
average of $q_{\text{calc.}}/q_{\text{obs.}}$				0.998
average deviation				0.007

a) The value of $q_{\text{calc.}}/q_{\text{obs.}}$ in parentheses was omitted in calculating the average. Those marked with an asterisk were given double weight.

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[*] Presented at Symposium on the Metal Complex Compounds held in November 11, 1952.

1) S. Shibata, M. Kishita and M. Kubo, *Nature*, **179**, 320 (1957).

2) S. Shibata and K. Sone, This Bulletin, **29**, 852 (1956).

3) L. Cambi and L. Szego, *Ber.*, **64**, 2951 (1931).

4) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, New York, (1952), p. 220.

5) L. Pauling, "Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, (1948), p. 119.

6) G. J. Bullen, *Nature* **177**, 537, (1956).

7) M. Kimura, *Chem, Researches*, **9**, 53(1951); S. Shibata and M. Kimura, This Bulletin, **27**, 485 (1954); M. Kimura, K. Kimura and S. Shibata, *J. Chem. Phys.*, **24**, 622 (1956).

and the minima below $q=70$ in the photographs. The measured q values of maxima and minima are given in Table I. The positions of some minima were not measured, because the period of the halos was very short. The visual intensity curve depicted in Fig. 3 was drawn from the measurement of the features of the halos and their positions so as to be represented by the following simplified intensity expression:

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

Here notations have their usual significances. On the non-sector photographs, the measurements of intensities were considerably difficult in the region of small q (2nd maximum and 2nd and 3rd minima) on account of the intense background of the photographs. Thus the error of this intensity measurement may affect the radial distribution curve. The use of r^2-sector photographs could probably eliminate such a difficulty. The portion of the intensity curve below $q=7$, which could not be observed, was necessary for the calculation of a correct radial distribution curve. Therefore from the observed curve, to which the unobservable part below $q=7$ was properly added, the radial distribution (R.D.) curve was calculated by use of the following formula:

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

Here the constant a was chosen to be 0.000545 and the summation was carried out up to $q_i=70$. Using the values of some interatomic distances obtained from the resulting curve, the theoretical intensity curves of several models were computed by the above formula. In this case, the ligands were assumed to be planar and to possess a symmetry C_{2v}. This assumption was made throughout in order to simplify this analysis. This assumption would be quite adequate if the contribution of the possible resonance structures of the ligand molecule were taken into account. The calculated $I(q)$ curves indicated that the intensity in the region of small q values (below about 13) was almost invariable, irrespective of whether the configuration of the calculated model was planar or tetrahedral. Accordingly, the observed part was continued with a dotted curve shown in Fig. 3 (upper curve) for the unobservable part of the intensity curve with reference to the calculated curve. The R.D. curve shown in Fig. 1 was calculated from this intensity curve in the same way as before. This curve is almost non-negative. The negative portions in the neighborhood of 3.5 Å and 5.3 Å are attributable to low frequency loops superimposed on this curve, and they seem to be due to the inaccuracy of the intensities for small q values (particularly to the 2nd maximum which was estimated much too high). However, no attempts were made to revise the visual curve because the positions of peaks presumably remain unchanged by this revision. The peaks of this curve could be assigned to the atomic pairs as given in Table II: thus peaks at 1.90, 2.84, 3.20 and

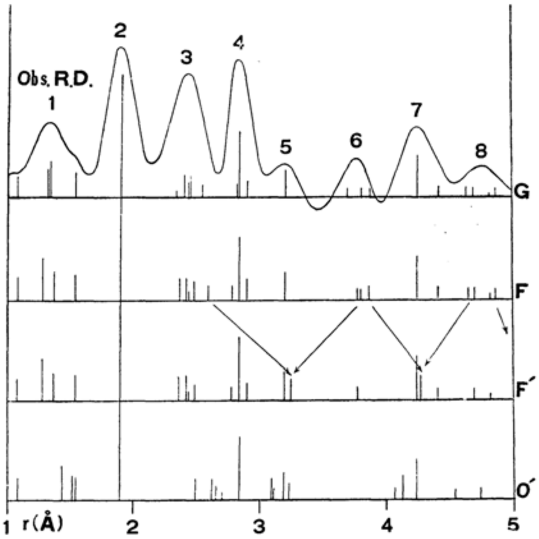

Fig. 1. The R. D. curves of bisacetylacetone-nickel(II). All the atomic pairs of each model are shown by the vertical bars in the computed R.D.

TABLE II

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

peak	distance (Å)	assignment[a)]
1	1.33	C_1O_1(3) C_1C_2(2) C_1C_4(2) CH(2)
2	1.90	NiO_1(10)
3	2.42	C_2O_1(2) C_4O_1(2) C_2C_4(1) C_1C_3(1) $O_1O_{2'}$(1)
4	2.84	NiC_1(5) C_3O_1(1) O_1O_2(1)
5	3.20	NiC_2(2)
6	3.74	$O_1O_{1'}$(1) $O_1C_{3'}$(1) C_1C_5(1)
7	4.25	NiC_4(3) C_5O_1(1)
8	4.75	$O_1C_{2'}$(1) $O_1C_{1'}$(1) $O_1C_{5'}$(1) C_4C_5(0)

a) These assignments correspond to the best models, G and F. Numbers in parentheses show approximately the relative magnitudes of Z_iZ_j/r_{ij}. The italicized atomic distances vary with the configuration of the chelate.

4.25 Å correspond to Ni–O_1*, Ni–C_1, Ni–C_2 and Ni–C_4, respectively. These four peaks are single or nearly single peaks because in these peaks one atomic pair has a predominant scattering power. Hence, it appears most likely that the values of these interatomic distances are reliable. Furthermore, from the R. D. thus obtained, the reasonable model of the ligand molecule was estimated as follows. When the structure of the ligand is assumed to be as mentioned above, the geometric consideration of the C_2–C_4 and the C_4–O_1 (the 3rd perk at 2.42 Å) and the C_1–C_5 (the 6th peak at 3.74 Å) with the above four distances leads to the model having the following parameters: $\angle O_1NiO_2=92°$, C_1–C_2=1.37 Å, C_1–O_1=1.26 Å and C_1–C_4=1.51 Å. Then the structure of the molecule is determined by the configuration depending on the angle between two ligand planes. Thus the calculation of the theoretical intensity curves for planar and rectangular twisted models showed that the planar model could well reproduce the observed curve but the rectangular model could not. Details will be described below. However it is to be noted for the above assignment that if the molecule takes a rectangular form, the 5th peak can also be assigned to the O_1–$O_{1'}$ as well as to the Ni–C_2 (this assignment leads to $\angle O_1NiO_2=99°$). Also the height of the 5th peak is fairly low. Therefore the assignment of this peak and the value of the Ni–C_2 distance were carefully taken into consideration.

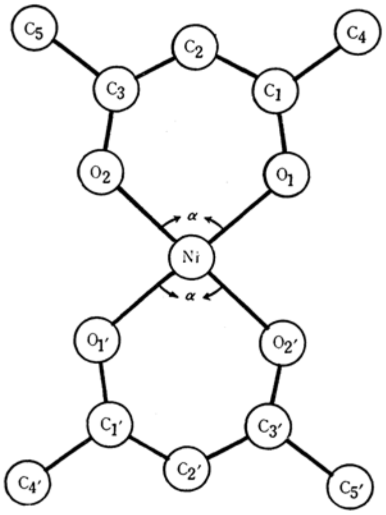

Fig. 2. The shape of the best model and the numbering of atoms.

Theoretical Intensity Curves

A calculation was made of the theoretical intensity curves for a number of models in order to determine the molecular structure in more detail and to check the accuracy of the interatomic distances obtained from the radial distribution method. However, in a complex molecule such as acetylacetone chelate, a complete determination of the molecular structure by the trial and error method would be very difficult on account of a large number of parameters. Therefore, in order to simplify this task, the present analysis was undertaken by the following assumption on the model. First, the interatomic distances of the Ni–O_1, Ni–C_1 and Ni–C_4, were taken to be equal to the most probable values obtained by R.D. method, i.e., 1.90, 2.84 and 4.25 Å, respectively. (The contribution of these atomic pairs to the total scattering power was about 40 %.) Secondly, the structure of the ligands was assumed to be the same as before (C_{2v} symmetry). Then, it follows from the assumptions that molecular models can be determined by four independent parameters for the ligand, i.e., $\angle O_1NiO_2$ (denoted by $\angle\alpha$), C_1–C_2, C_1–C_4 and Ni–C_2 and the angle between the planes of the two ligands. As regards the configuration of the molecule, two cases of a planar form and a rectangular twisted form (including the tetrahedral form) were taken into account. Thus, the theoretical intensity curves were calculated of a large number of carefully selected models (about eighty) with various values for the above parameters. The values of the parameter $\angle\alpha$ was taken over the range from 84° to 110°, that of the C_1–C_2 from 1.32 Å to 1.57 Å. The value of the Ni–C_4 was taken to be 3.20 Å (the value obtained from the R.D.) and 3.10 Å (This smaller value makes the internuclear strain of the ligand smaller in the case of $\angle\alpha$=tetrahedral angle.) The length of C_1–C_4 was taken to be 1.54 Å and 1.51 Å, (because these values are quite reasonable and also because this bond nearly bisects $\angle O_1C_1C_2$ when C_1–C_4 is assumed to take these definite values.) These calculated intensity curves contain the contributions from all the atomic pairs, the pairs pertaining to hydrogen being

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* The notation "Ni-O_1" also means Ni-$O_{1'}$, Ni-O_2 and Ni-$O_{2'}$ by the assumed symmetry of ligand. The situation is the same in the case of other atomic pairs.

ignored except for H–C bondings which were assumed to be 1.08 Å.

The calculation of the intensity curves was performed with the aid of Remington Rand punch cards. When these intensity curves are compared with each other with respect to the variation in the positions and the relative intensities of maxima and minima with the change of parameters, the following facts can be found. In general, the theoretical curves are particularly sensitive to the parameters, ∠α and C_1–C_2. The maxima and these minima sensitive to the parameters are the 8th, 9th, 11th and 12th maxima, and the 10th and 11th minima. The parameter C_1–C_4 does not seriously affect the intensity curve even when this distance differs from 1.54 and 1.51 Å so long as the Ni–C_4 distance does not change. It was also found that the long interatomic distances (greater than 5 Å such as O_1–$C_{4'}$, C_1–$C_{1'}$, C_1–$C_{2'}$, C_1–$C_{4'}$, C_1–$C_{5'}$, C_2–$C_{4'}$, etc.) contribute to the appearance of the 4th and 6th minima. (This contribution is about 7 %.) Some of the intensity curves are shown in Fig. 3.

TABLE III
MODELS FOR THE THEORETICAL INTENSITY CURVES

model	∠α	C_1–C_2 (Å)	C_1–O_1 (Å)	C_1–C_4 (Å)	Ni–C_4 (Å)	configuration
A	88°	1.32	1.23	1.54	3.20	planar
B	90°	〃	1.26	〃	〃	〃
C	〃	1.42	1.20	〃	〃	〃
D	92°	1.37	1.26	〃	〃	〃
E	〃	1.47	1.21	〃	〃	〃
F	94°	1.37	1.28	1.54	〃	〃
F′	〃	1.37	1.28	〃	〃	rectangular
G	96°	1.32	1.34	〃	〃	planar
G_t	〃	〃	〃	〃	〃	〃
$G_{1.51}$	〃	〃	〃	1.51	〃	〃
H	〃	1.42	1.28	1.54	〃	〃
I	〃	1.52	1.23	〃	〃	〃
J	98°	1.32	1.37	〃	〃	〃
K	〃	1.37	1.34	〃	〃	〃
K′	〃	〃	〃	〃	〃	rectangular
L	〃	1.47	1.28	〃	〃	planar
M	100°	1.37	1.37	〃	〃	〃
M′	〃	〃	〃	〃	〃	rectangular
N	108°	1.52	1.40	〃	〃	planar
O	110°	1.52	1.43	〃	〃	〃
O′	〃	1.52	〃	〃	3.10	rectangular (nearly tetrahedral)
P	96°	1.32	1.31	〃	〃	planar
Q	100°	1.37	1.34	〃	〃	〃
Q′	〃	1.37	〃	〃	〃	rectangular
R′	110°	1.52	1.40	1.54	〃	rectangular (nearly tetrahedral)

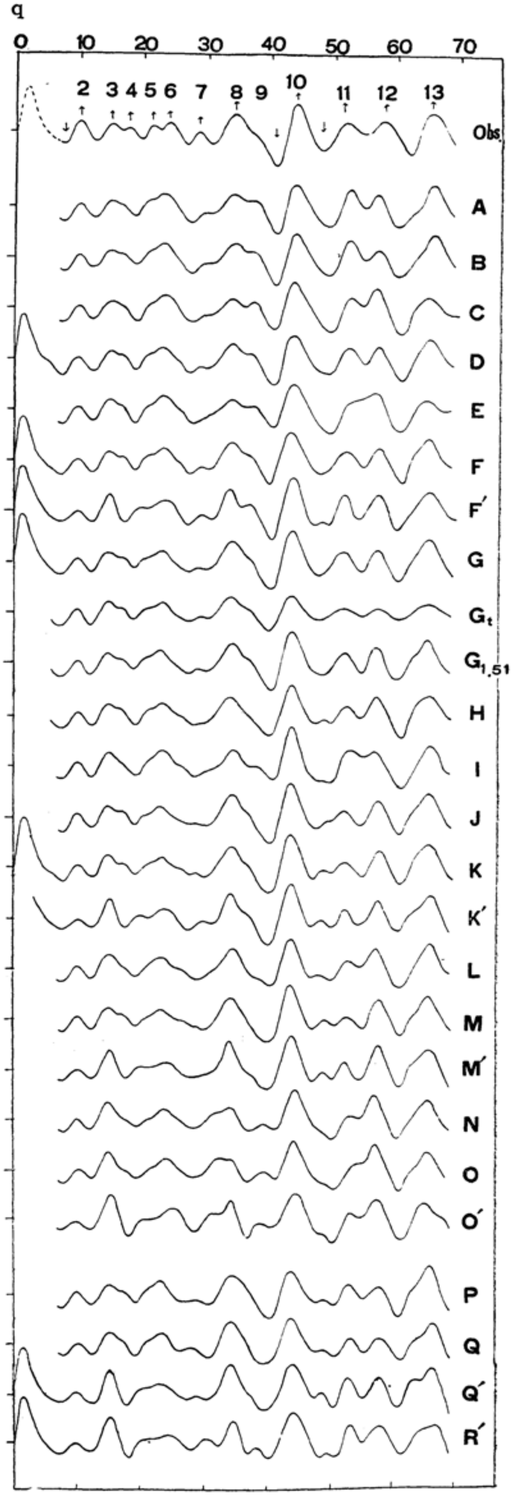

Fig. 3. The observed and the theoretical intensity curves.

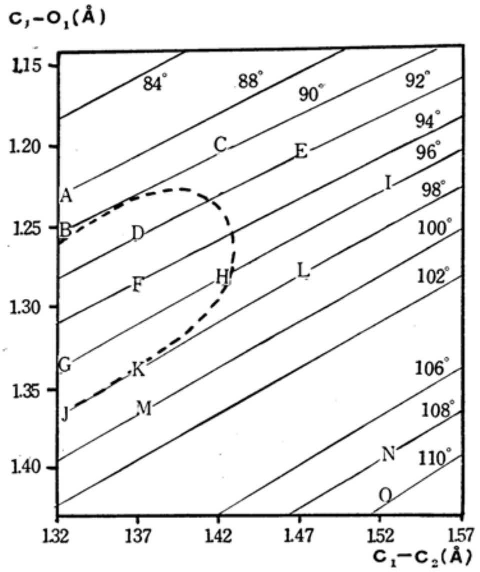

Fig. 4. Parameter chart. This chart shows the case of the parameter Ni–C_2 =3.20 Å. The positions of letters indicate the parameters of the models for which intensity curves are shown in Fig. 3.

The parameters of the corresponding models are listed in Table III. The curve A is unsatisfactory since the 8th maximum is too low and the 9th maximum is too high. Curve B is somewhat unsatisfactory in the same points as for the curve A as well as in the relative intensities of the 11th and 12th maxima. This model gives the lower limit of $\angle\alpha$. The curve C is unsatisfactory, because the 8th and 9th maxima (The observed 9th shelf was so faint that its position could not be measured definitely.) and the 10th minimum (too shallow) are not well reproduced. The curve D is acceptable. This model corresponds to the most probable one estimated from the R.D. curve. The curve E is unacceptable because of the features of the 7th, 8th and 9th maxima, the relative depths of the 10th and 11th minima and the features of the 11th and 12th maxima. The curve F is satisfactory. The curve G is also satisfactory and an agreement with the observed is better than the curve D in regard to the feature of the 9th shelf and the positions of the 11th and 12th maxima and the 11th minimum. The comparison of the curve G with the curve $G_{1.51}$ shows that the parameter C_1–C_4 is sensitive only to the relative heights of the 11th and 12th maxima. The curve H is somewhat unsatisfactory and provides the upper limit of C_1–C_2 since the 7th and 9th maxima are too faint. The curve I with C_1-C_2=1.52 Å is also unsatisfactory because of the feature of the 7th, 8th and 9th maxima and the relative depths of the 10th and 11th minima. The curve J is somewhat unsatisfactory because the relative heights of the 11th and 12th maxima deviate from observations and it provides the upper limit of $\angle\alpha$. The curve K is unacceptable because of the feature of the 11th maximum. The curve L is unacceptable. Model M having $\angle\alpha$ larger than 98° is unacceptable. Model N and O having $\angle\alpha$ almost equal to the tetrahedral angle are definitely unacceptable since they require the intensity curve which is discrepant from the observed curve particularly in regard to the range of q from 30 to 60. In models having large $\angle\alpha$, C_1–C_2 cannot be taken smaller than the above value because C_1–O_1 becomes unreasonably longer than 1.42 Å. The above models are indicated in a parameter chart, Fig. 4. Although a number of intensity curves were also calculated for the corresponding models mentioned above with Ni–C_2=3.10Å, these curves did not agree with the observed one. Some of them are shown in Fig. 3. (see curve P and Q.) For example, if the curve P is compared with the corresponding curve G, it is found that the shortening of Ni–C_2 makes the 9th maximum lower and shifts the 11th maximum to a larger q value. In the present analysis the value of Ni–C_4 was also varied, but better agreement could not be obtained. The calculations show that the parameter Ni–C_4 is sensitive only to the relative heights of 5th and 6th maxima. If the molecule takes a configuration with one ligand plane at right angles to the other ligand plane, such as in models F′, K′, M′ and O′ (The last is a tetrahedral model.), in general, the features of the 3rd and 4th (disappearing) maxima and the position of the 5th maximum disagree remarkably with those of the observed curve. It is to be noted that these changes occur in the range below q=30, because in regard to other acetylacetone chelates the configurations of these chelates can easily be determined by only the intensities in this part. Quite similar kinds of behavior are seen in the case of the models having Ni–C_2=3.10 Å such as models Q′ and R′. Therefore, all the rectangular models including the tetrahedral models are ruled out*.

This conclusion was also confirmed by the computed R.D. shown by the vertical bars below the observed R.D. in Fig. 1. The positions of the bars show the interatomic distances; the heights of the bars are drawn proportional to Z_iZ_j/r_{ij} of the respective atomic pairs. The upper computed R.D. corresponds to the model G which is in good agreement with the observed R.D. as regards the positions and the areas of the peaks. The R.D. F also agrees well with the observed R.D., whereas the computed R.D. F′ is in poor agreement with the observed R.D. with respect to the 5th, 6th and 8th peaks because the ratio of the area of each of these peaks to the sum of the heights of the corresponding bars extremely deviates from the ratio on other peaks. Here oblique arrows connect corresponding atomic pairs. Accordingly the planar model is superior to the rectangular twisted models. The lower R.D. corresponds to the tetrahedral model O′ and the disagreement with the observed R.D. is much enhanced. If the molecule takes the tetrahedral form, the 5th peak in the observed R.D. would rise and the 6th peak would disappear.

It must be mentioned also that the effect of molecular vibration was not taken into account in the above description because it did not seriously affect the features of the intensity curve below $q=70$. This effect was included in the calculation with the following values for root mean square amplitude, $\langle l_{ij}^2\rangle_{Av}^{1/2}$, 0.07** Å for Ni–O, 0.06 Å for C–C, 0.05 Å for C–O, and 0.08 Å for C–H, by use of the formula:

$$I(q)=\sum_{i\neq j}(Z_iZ_j/r_{ij})\exp(-bq^2)\sin(\pi q r_{ij}/10),$$
$$\text{where } b=(\pi^2/200)\langle l_{ij}^2\rangle_{Av}$$

As an example, curve G_t is shown in Fig. 3. From the comparison of curve G_t with curve G, it was found that this effect did not affect the positions and the relative intensities of the maxima and the minima except the introduction of simple intensity damping but that this effect produced a slight change in the relative intensities only for the 10th and 11th minima and the 11th and 12th maxima.

Results

The computation of intensity curves showed that the general appearance of the the photographs was well reproduced by planar model. In the parameter chart, Fig. 4, the dashed line separates satisfactory models from unsatisfactory ones with due regard to atomic vibrations. The q values of the maxima and the minima for best model are listed in Table I for comparison with those of the observed maxima and minima. From the analysis described above, the molecule of bisacetylacetone-nickel(II) was found to have the planar configuration, with the following parameters: $\text{Ni–O}_1=1.90$ Å, $\text{Ni–C}_1=2.84$ Å, $\text{Ni–C}_2=3.20$ Å, $\text{Ni–C}_4=4.25$ Å (These values were obtained from the R.D. and the correctness of these values were checked by the calculations of the theoretical intensity curves.), $\angle\alpha=94\pm4°$, $\text{C}_1\text{–C}_2=1.37\pm0.05$ Å, $\text{C}_1\text{–O}_1=1.30\pm0.06$ Å, and $\text{C}_1\text{–C}_4=1.51$ Å$\sim$1.54 Å. Although it is impossible to determine accurately C–C and C–O distances on account of the complexity of the molecule, it is an important conclusion that the chelate has a planar configuration with Ni–O distance equal to 1.90 Å.

Discussion

It is convenient to discuss the results under two headings: (i) bond lengths and bond types, and (ii) stereochemical configuration.

(i) *Bond lengths and bond types*. It must, at first, be mentioned that the observed Ni–O distance of 1.90 Å leads to the radius 1.24 Å for Ni(II) in square configuration with coordination number 4, in contrast with the known radius, 1.39 Å in octahedral configuration, although Pauling[8] estimated the square radius of Ni(II) to be 1.21 Å from the octahedral radius.

The observed Ni–O distance is slightly greater than the sum of the covalent radius of oxygen (0.66 Å) and the metallic radius[9] of nickel with a coordination number 8 (1.22 Å), but is in good agreement with the sum of the covalent radius of oxygen and the metallic radius[9] of nickel with a coordination number 12 (1.25 Å) or the neutral atomic radius[10] (1.24 Å). This may afford an evidence for the Ni–O bond is fairly covalent. On the

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* The intensity curves were also calculated for the mixture of the planar and the rectangular models at the ratio of 25～75%, but these curves did not agree with the observed one.

** This value was obtained from a preliminary study on cobalt(II) acetylacetone chelate by the sector-microphotometer method. Also the values for non-bonding atomic pairs were estimated using the data and the calculated values on other compounds.

[8] Ref., 5, chapt. 5.

[9] Ref., 5, chapt. 11.

[10] N. V. Sidgwick, "The Chemical Elements and their Compounds" Vol. II, Oxford Univ. Press, (1950), p. 1317.

other hand, if Ni–O bond were purely ionic, the distance would be predicted from a simple calculation* to be about 2.2 Å. Such examples are NiO, $NiSO_4 \cdot 6H_2O$, and $NiSO_4 \cdot 7H_2O$[11], in which Ni–O distances have actually been found to be equal to 2.0~2.2 Å. Because no structure of chelates containing an Ni–O bond has yet been studied in detail, the Ni–O bond length observed for bisacetylacetone-nickel (II) cannot directly be compared with other data. The recent data on $Ni(CH_3COO)_2 \cdot 4H_2O$[12] gave about 2.1 Å for Ni–O, but this bond may be considered to be essentially ionic.

Bisacetylacetone-nickel(II) chelate possesses non-ionic properties and a considerable stability. The non-ionic properties of the chelate, i.e., the volatility and the solubility in organic solvents, may naturally be explained by the covalent character of the Ni–O bonds described above. It is noticed that the Ni–O bond length is almost equal to the covalent bond length, although the electronegativity difference between Ni and O atoms leads to an ionic character of about 50 per cent. for the Ni–O bond. This is presumably due to the formation of double bond by use of some of the $d\pi$-type orbitals of the nickel atom. On the other hand, the stability of the chelate is attributable to the great strength of dsp^2 hybrid orbitals of nickel atom. This seems to be also due to the contributions of many resonance structures of the ligand molecule which are due to the conjugation among $2p\pi$ orbitals of ligand atoms and $3d\pi$ or $4p\pi$ orbitals of the nickel atom. Further, the fact that the chelate forms the planar rather than the tetrahedral configuration makes more possible the conjugation over the whole molecule consisting of eleven members, resulting in the enhanced stability of the chelate.

(ii) *Stereochemical configuration.* In general, it is well known[13] that the quadricovalent complexes of copper(II) are invariably planar, whereas those of nickel(II) and cobalt(II) may be either planar or tetrahedral depending on the ligand. It is generally found further that with nickel(II) complexes the choice of these configurations is particularly sensitive to the electronegativity of the donor atoms. In other words, Ni(II) complexes with the donor atoms, N or S take a planar configuration and those with O take the tetrahedral one. No planar configuration of the Ni(II) complexes having the donor atoms of O has been found experimentally until the present study was made on bisacetylacetone-nickel(II) chelate.

According to magnetic measurement[1,3], bisacetylacetone-nickel(II) chelate is paramagnetic. From this result, Pauling presumed that Ni(II) has the tetrahedral orbitals which are constructed from sp^3 hybridization. The present result is contradictory to his presumption, although it seems likely that magnetic data do not necessarily exclude the planar form because the promotion of a $3d$ electron to a $4p$ orbit makes the chelate paramagnetic even in $3d4s4p^2$ planar configuration and also the use of $4d$ orbit makes it likewise paramagnetic in $4s4p^24d$ planar configuration as suggested by Huggins[14].

However, the present result that the chelate takes the planar rather than tetrahedral configuration seems to be not surprising because dsp^2 bonds are stronger than sp^3 bonds and moreover the conjugation over the whole molecule in favor of the planar form probably makes the chelate more stable. Some energy may be, of course, required when the Ni(II) takes the electron configuration of $3d4s4p^2$ with paired electrons promoted in one of the $3d$ orbitals or an unpaired electron promoted in one of the $4p$ orbitals. However, such promotion energy will probably be compensated by the stabilization energy acquired by taking this configuration.

It is interesting to note for the above contradiction that the present experiment deals with free molecules at a high temperature, while magnetic measurement and other experiments deal with the chelate in the solid state at room temperature. If the presumption of Pauling is true, it is possible that the configuration of the chelate would vary with the phase change (or temperature**), taking planar in gaseous state and tetrahedral in solid state, because the energy difference between

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

[11] R. W. G. Wyckoff, "Crystal Structure", Interscience Publishers, New York, Vol. I (1948), Vol. II (1951).

[12] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 609 (1953).

[13] Ref., 4, p. 278.

[14] M. L. Huggins, *J. Chem. Phys.*, **5**, 527 (1937).

** In genaral, the configuration of the chelate is distinguishable by the color of the chelate. Although it is doubtful whether the following is related to the above or not, it is actually observed in experiment that the green color of the chelate was slightly tinged with yellow on heating. (Ref., 5, p. 122).

the planar and the tetrahedral structures is very small. Recently it is found that, for example, bis-N-methylsalicylaldimine-nickel(II)[15] behaves in a similar manner although all such chelates hitherto reported have both N and O atoms as donors. In order to clarify the above suggestion and the discrepancy between the conclusions from the magnetic data and the electron diffraction data on bis-acetylacetone-nickel(II), the following two investigations are very desirable; the complete determination of the structure of the chelate on single crystals by X-ray method*** and the measurement of the magnetic moment of the chelate in gaseous state. The latter will also give the information on the electronic state of Ni(II) atom which has the planar orbitals.

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[15] S. Fujii and M. Sumitani, *Science Repts. Tôhoku Univ., First Series*, **37**, 49 (1953); J. B. Willis and D. P. Mellor, *J. Amer. Chem. Soc.*, **69**, 1237 (1947).

*** Our preliminary investigation by powder method showed that the chelate has probably the tetrahedral configuration.