Studies on the Structure of Bisacetylacetone-Nickel(II) by the X-ray Powder Method

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Pauling[1] proposed the tetrahedral configuration of bisacetylacetone-nickel(II) on the basis of the paramagnetic property of the complex with the aid of his theory. On the other hand, experiments[2,3] by electron diffraction of gas gave the result that the molecule assumes a planar configuration. If it is noted for this contradiction that the electron diffraction study dealt with free molecules at high temperature (about 170°), whereas the magnetic measurement was made on the solid at room temperature, it seems likely that the configuration of the molecule depends on the environment of a molecule[*1].

According to the recent theoretical consideration[4], however, the magnetic data (paramagnetic) are not necessarily conclusive for the choice to be made between the tetrahedral and the planar arrangement. Therefore the X-ray method has been undertaken to afford a more direct evidence for the configuration of a bisacetylacetone-nickel(II) molecule in the solid state at room and high temperatures. Although X-ray analysis on single crystals is desirable for the complete determination of the structure of the molecule, it was difficult to prepare single crystals of an appropriate size of an anhydrous nickel complex. Therefore, investigations were carried out by the powder method. The powder patterns of nickel complex were compared with those of copper and zinc complexes.

Experiments and Results

The powder photographs[*2] of copper, nickel and zinc complexes were prepared by the use of Cu-$K\alpha$ radiation from the samples enclosed in a capillary tube made of glass. Samples recrystallized from ethanol were furnished by Dr. Sone. Anhydrous compounds were prepared by sublimation in vacuo; hydrates[*3] were obtained by leaving them to stand in moist air. The patterns thus obtained are shown in Fig. 1.

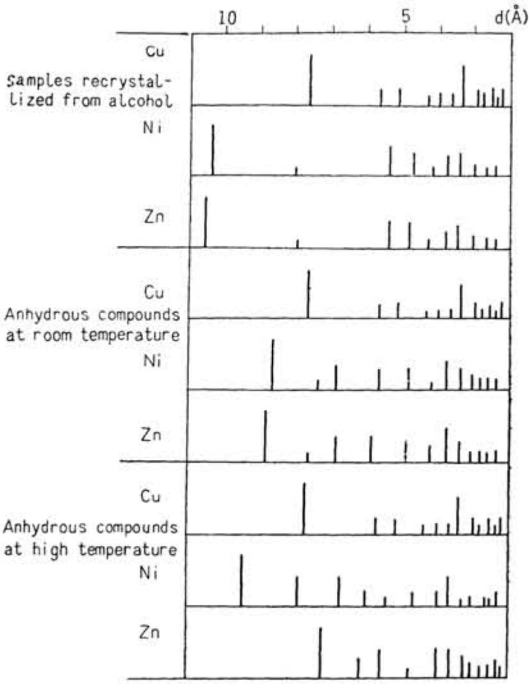

Fig. 1. The powder patterns of Cu, Ni and Zn acetylacetones.

1) Bisacetylacetone-copper(II). The sample recrystallized from ethanol and that sublimed in vacuo, both of which were dark blue in color, gave identical powder patterns. The sample heated up to about 200° also gave the same powder patterns.

2) Bisacetylacetone-nickel(II). The sample recrystallized from ethanol and the hydrate

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

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

3) S. Shibata, This Bulletin, to be published shortly.

[*1] From this point, magnetic measurements have been made on the solid at high temperature, but the results showed no indication of the change in magnetic moment with temperature. (Ref. 2).

4) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332: Y. Kuroda and K. Ito, *J. Chem. Soc. Japan, Pure Chem Sect.*, **76**, 762 (1954).

[*2] The patterns of cobalt(II) complexes were also taken by the use of Fe-$K\alpha$ radiation. The results showed that pink hydrate and red-violet anhydrate were isomorphous with the corresponding nickel(II) complexes, respectively.

[*3] Only the copper(II) complex was not hydrated and did not contain alcohol when it was recrystallized from an alcoholic solution.

thereof[*4], both of which were blue in color, gave the identical patterns. On heating at about 130° the green color of the anhydrous compound changed into yellow-green, which color persisted up to about 170°. These two samples showed different powder patterns as shown in Fig. 1, suggesting that a change was taking place in the crystal structure. They are designated as the room and the high temperature modification, respectively. The green anhydrous compound (the room temperature modification) was readily hydrated in moist air, but the yellow-green anhydrous compound (the high temperature modification) was fairly stable even in moist air. The blue hydrate[*5] was reversely converted into a green anhydrous compound at about 80°.

TABLE I

INTERPLANAR SPACINGS FROM POWDER PATTERNS*

$Cu(C_5H_7O_2)_2$		$Ni(C_5H_7O_2)_2$		$Zn(C_5H_7O_2)_2$	
d(Å)	I	d(Å)	I	d(Å)	I
7.61	vs	8.66	vs	8.82	vs
5.66	w	7.41	vw	7.60	vw
5.14	w	6.82	mw	6.85	m
4.35	vw	5.67	mw	5.86	mw
3.99	w	4.80	mw	4.88	mw
3.60	w	4.18	vw	4.22	w
3.37	ms	3.78	m	3.73	m
2.94	w	3.39	mw	3.40	mw
2.78	vw	3.07	w	3.09	w
2.50	w	2.83	w	2.82	w
2.34	vw	2.61	w	2.63	vw
2.22	w	2.38	w	2.35	w
2.00	w				

* The lines which may be due to an impurity such as a hydrate were not listed.

3) Bisacetylacetone-zinc(II). White bisacetylacetone-zinc(II) gave three different patterns i. e., one for the hydrate, which was found to be isomorphous with the hydrate of nickel complex, and two for the anhydrous compound. This behavior with changing temperature was quite similar to the case of bisacetylacetone-nickel(II).

Discussion

The crystal structure of bisacetylacetone-copper(II) has already been determined by Koyama et al.[5] by X-ray analysis on a single crystal. The result showed that the complex takes a planar (square) configuration[*6]; a copper atom completes a distorted octahedron. On the other hand, the tetrahedral nature of four-covalent zinc(II) complexes is established from theoretical and experimental[6] basis. When the powder patterns of anhydrous copper, nickel and zinc complexes are compared with one another, the patterns of the room temperature modification of the nickel complex are clearly distinguishable from those of the copper complex, while it is essentially identical with those of the zinc complex. The interplanar spacings are listed in Table 1. Accordingly, it seems to be sure that the bisacetylacetone-nickel(II) has a tetrahedral configuration rather than a planar one, in agreement with the deduction by Pauling.

In order to investigate a possible change in the structure of bisacetylacetone-nickel (II) with temperature, the powder patterns of anhydrous copper, nickel and zinc complexes were taken at high temperature, but these patterns were different from one another. The pattern of high temperature modification of the anhydrous nickel complex seems to show a possibility of the change in the molecular structure of this complex, but does not simply permit a choice between a tetrahedral and planar coordination.

Recently Bullen[7] investigated the crystal structure of anhydrous bisacetylacetone-nickel(II) by X-ray analysis on a single crystal, determined the lattice constants, and reported the presence of trinuclear molecules in the crystal. Although he did not definitely elucidate the molecular structure of the complex, the short distance between nickel atoms would favor the planar configuration of the complex. On the other hand, it was found that the interplanar spacings calculated by the use of his lattice constants are more consistent with those of the high temperature modification than with those of room temperature modification of this complex. Therefore, it is possible that the nickel complex of the high temperature modification may have the planar configuration, although the determination is not complete. If this

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[*4] Experiments showed that the hydrate contains two molecules of water per one molecule of the complex.

[*5] It seems likely that, in the hydrate, water molecules are loosely coordinated to metal atoms and presumably from an octahedral configuration about the central metal atom with other ligand atoms and are easily removed on drying at high temperature.

5) H. Koyama, Y. Saito and H. Kuroya, *Journal of the Institute of Polytechnics, Osaka City University*, **4**, Series C, 43, (1953).

[*6] The square planar configuration of a free molecule of bisacetylacetone-copper(II) has been indicated also by electron diffraction investigation. (S. Shibata and K. Sone, This Bulletin, **29**, 852 (1956)).

6) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, New York, (1952), p. 245. J. C. I. Liu and J. C. Bailar, *J. Am. Chem. Soc.*, **73**, 5432 (1951); H. Koyama and Y. Saito, This Bulletin, **27**, 113 (1954).

7) G. J. Bullen, *Nature*, **117**, 537 (1956).

is the case, this fact indicates that the configuration of bisacetylacetone-nickel(II) varies with temperature.

Conclusion

X-ray powder pattern method led to the result that four-covalent bisacetylacetone-nickel(II) takes a tetrahedral configuration in agreement with the presumption of Pauling. On the other hand, a previous experiment by electron diffraction showed that the free molecule of this complex has a planar configuration. Thus, these experimental evidences lead to the following interesting inference: the configuration of anhydrous bisacetylacetone-nickel(II) varies with the change of the phase from gas to solid (or with temperature). This is evidently due to the fact that the energy difference between the tetrahedral and planar configuration is quite small.

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