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# Model Complexes of Catalysts for Asymmetric Hydrogenation. I. Crystal Structure of $\beta$ -Cyanoethyl(D(-)-erythro-1,2-diphenyl-2-hydroxyethyl-amine)bis(dimethylglyoximate)cobalt

Yuji OHASHI, Yoshio SASADA, Yasuhisa TASHIRO, Yoshiaki OHGO, Seiji TAKEUCHI, and Juji YOSHIMURA

*Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*

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It has recently been shown that the complexes of bis(dimethylglyoximate)cobalt(II) and optically active amine (abbreviated to  $\text{Co}(\text{DMG})_2$ -amine) catalyze asymmetric hydrogenation of olefins,  $\alpha$ -diketones and  $\alpha$ -keto carboxylic esters.<sup>1-5)</sup> Optical yields vary with the amine and solvent. From chemical consideration and CD and NMR spectra, these complexes seem to have a structure<sup>5)</sup> as shown in Fig. 1. The  $\text{Co}(\text{DMG})_2$  plane is twisted by hydrogen bonding between one of the oxygen atoms of DMG and the hydroxyl group of amine. The direction of this twist is determined by the absolute configuration of the optically active amine. Asymmetry around the cobalt atom caused by the twisted plane is transferred to the products at a certain stage of catalytic reaction. The present work has been undertaken to examine this hypothesis and to give a structural explanation to the mechanism of

asymmetric hydrogenation.

The crystal structure of the title compound  $\text{C}_{25}\text{H}_{33}\text{N}_6\text{O}_5\text{Co}$  was determined by X-ray method. Crystal data;  $M=556.51$ , monoclinic with  $a=13.31$ ,  $b=8.84$ ,  $c=23.90$  Å,  $\beta=108.0^\circ$ ,  $V=2673.2$  Å<sup>3</sup>,  $Z=4$ . The density calculated is  $1.37$  g/cm<sup>3</sup>, while that measured by flotation is  $1.38$  g/cm<sup>3</sup>. Systematic absence of reflections is  $0k0$  for  $k=2n+1$ , the space group being  $P2_1$ . The molecular arrangement, however, seems to have an approximate  $P2_1/c$  symmetry because  $h0l$  reflections are very weak for  $l=2n+1$ . A total of 2127 independent reflections were collected on Weissenberg photographs using  $\text{CuK}\alpha$  radiation. Intensities were measured visually. Correction for Lorentz and polarization factors was applied as usual but not that for absorption.

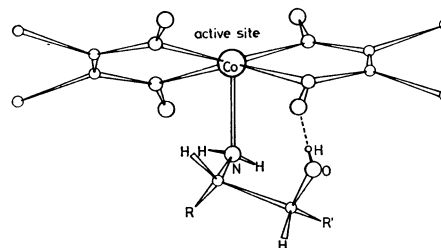


Fig. 1.

1) Y. Ohgo, S. Takeuchi, and J. Yoshimura, *This Bulletin*, **44**, 583 (1971).

2) Y. Ohgo, S. Takeuchi, and J. Yoshimura, Presented at the 19th Symposium on Organometallic Chemistry, October, 1971, Preprints p. 55.

3) S. Takeuchi, Y. Ohgo, and J. Yoshimura, Presented at the 25th Annual Meeting of Chemical Society of Japan, October, 1971. Preprints p. 410.

4) Y. Ohgo, Y. Natori, and J. Yoshimura, Presented at the 26th Annual Meeting of Chemical Society of Japan, April, 1972. Preprints p. 1010.

5) S. Takeuchi, Thesis, Tokyo Institute of Technology (1972).

At first an approximate  $P2_1/c$  symmetry was tentatively assumed. Atomic positions were easily obtained by the heavy atom method and refined by block-diagonal least-squares. After three cycles of the least-squares, an electron density was calculated, where the peaks for the amine were broader and lower than those of the others. This suggests that in the two crystallographically independent complexes the  $\beta$ -cyanoethyl and the  $\text{Co}(\text{DMG})_2$  groups are related almost strictly by a  $c$ -glide plane, but not the amine ligands. Thus a trial structure based on  $P2_1$  was constructed, in which the atomic parameters of the former two groups were taken from the refinement based on  $P2_1/c$ , those of the optically active amine being obtained by resolving the average structure. Further refinement was carried out by block-diagonal least-squares. Anisotropic temperature factors were taken into account for the cobalt atom and all other atoms were constrained to isotropic motion. The final  $R$  factor was 0.14. The estimated standard deviations of bond distances and angles are  $0.02$ – $0.04$  Å and  $2$ – $3^\circ$ , respectively.

Structures of two crystallographically independent complexes are identical to each other within standard deviations. Figure 2 shows one of these complexes

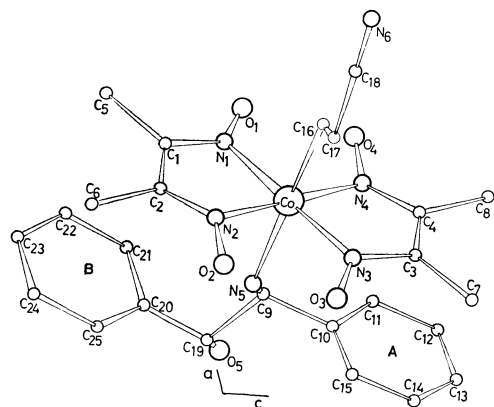


Fig. 2.

projected along the  $b$  axis. The  $\text{Co}(\text{DMG})_2$  groups are planar within standard deviations except for the methyl groups. Two methyl groups above the two benzene rings are slightly shifted upward to avoid short contact with the benzene rings. Figure 3 shows the complex viewed along  $\text{N}(1)$ – $\text{N}(2)$ . The plane of  $\text{Co}(\text{DMG})_2$  except the methyl groups makes angles of  $13^\circ$  and  $15^\circ$  with the benzene ring A and B, respectively. The distances from the centers of the rings to the  $\text{Co}(\text{DMG})_2$  plane are  $3.59$  Å for A and  $3.91$  Å for B. The average  $\text{Co}$ – $\text{N}$  distance and  $\text{N}$ – $\text{Co}$ – $\text{N}$

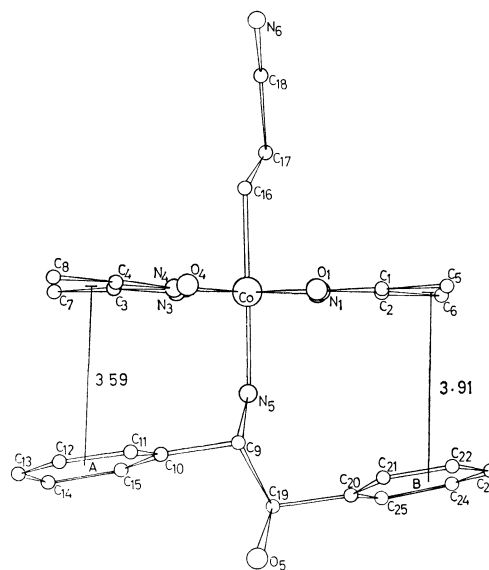


Fig. 3.

angle for the equatorial ligands are  $1.89$  Å and  $82^\circ$ , respectively. The axial  $\text{Co}$ – $\text{N}$  distance is  $2.08$  Å and the  $\text{Co}$ – $\text{C}$  distance is  $2.04$  Å. These distances and angles are close to those of alkyl cobaloxime.<sup>6)</sup> The axial  $\text{Co}$ – $\text{N}$  and  $\text{Co}$ – $\text{C}$  bonds make angles of  $84^\circ$  and  $85^\circ$  with the  $\text{Co}(\text{DMG})_2$  plane, respectively. The other distances and angles also agree with the values published.

As to the conformation of amine,  $\text{O}(5)$  and  $\text{N}(5)$  atoms are *trans* as shown in Fig. 3. Thus contrary to expectation, there is no hydrogen bonding between the oxygen atom of DMG and the hydroxyl group of amine. The hydroxyl group does not make any hydrogen bonding with neighbouring complexes.

Any distance between non-bonded atoms, within the complex and between neighbouring ones, is not abnormally shorter than the usual van der Waals contact.

The structure of the complex obtained here is different from the assumed structure shown in Fig. 1. However, it does not seem that the mechanism of asymmetric induction could be revealed with the present structure, since the asymmetry of amine would have no effect on active site of the cobalt atom. An alternative explanation might be as follows. The complex coordinated by the amine of *gauche* conformation probably exists in solution, which might catalyze asymmetric hydrogenation.

6) P. G. Lenhert, *Chem. Commun.* **1967**, 980.