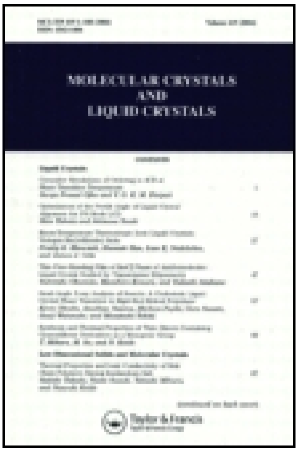

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CRYSTALLINE-STATE *TRANS-CIS* PHOTOISOMERIZATION OF COBALOXIME COMPLEXES

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Abstract It was observed by X-ray single crystal analysis that *trans*-2-buten-1-yl cobaloxime complex with pyridine or 4-bromopyridine as a axial ligand isomerizes to the *cis* isomer with retaining the single crystal form on exposure to a Xe lamp. The complex with 3-chloropyridine or methylsulfide as a axial ligand did not show the isomerization. The reaction cavities for the *trans*-2-butenyl groups calculated from four crystal structures showed that those of reactive crystals are significantly larger than those of non-reactive ones.

INTRODUCTION

The crystalline-state reaction proceeds without degradation of the single crystal form, so that the structures at the intermediate stages can be observed by X-ray analysis and the relationship between the crystal structure and the reactivity can be obtained. Two types of crystalline-state reactions of cobaloxime complexes have been found; the racemization of chiral alkyl groups[1, 2, 3, 4] and the isomerization of the 2-cyanoethyl to 1-cyanoethyl group in some cobaloxime complexes.[5] Recently we reported that the *trans*-2-butenyl group in a cobaloxime complex with pyridine as a axial ligand, **1**, isomerize to the *cis* isomer in the crystalline-state by irradiation with a Xe-lamp.[6] In this paper, the structures and the reactivities of the 4-bromopyridine, **2**, 3-chloropyridine, **3** and methylsulfide, **4**, complexes (FIGURE 1) will be discussed.

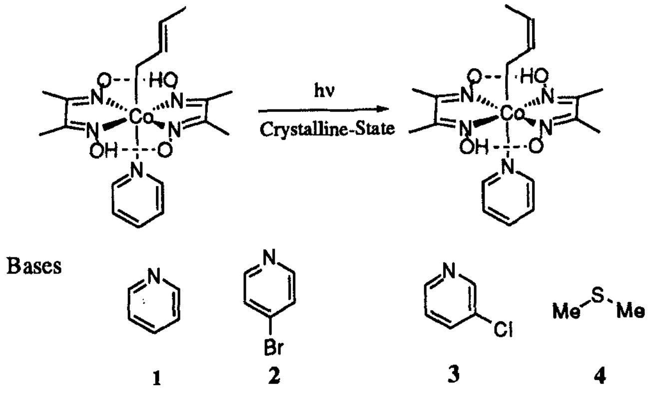


FIGURE 1 *Trans-cis* photoisomerization of *trans*-2-butenyl cobaloximes.

STRUCTURE AND REACTIVITY

4-Bromopyridine Complex

Crystal data are as follows; $C_{17}H_{25}BrCoN_5O_4$, Mr = 502.26, orthorhombic, space group *Cmca*, $Z = 8$, $a = 11.881(5)$, $b = 13.283(5)$, $c = 26.459(5)$ Å, $V = 4176(3)$ Å^3, $Dx = 1.601$ Mgm^{-3}, $\mu = 2.768$ mm^{-1}. The structure was solved by using the structure of pyridine complex as an initial structure. Final $R(F)$ and $wR(F^2)$ values became 0.050 and 0.111, respectively. Since the molecules lie on the mirror plane normal to the *a* axis as shown in FIGURE 2, a half of the molecule is crystallographically independent. FIGURE 3 shows the molecular structure with the numbering of atoms. The Co, C8, N3, Br and C7 atoms lie on a mirror plane, which passes through the long axis of the cobaloxime moiety. This mirror plane brings about a disordered structure of the *trans*-2-butenyl group.

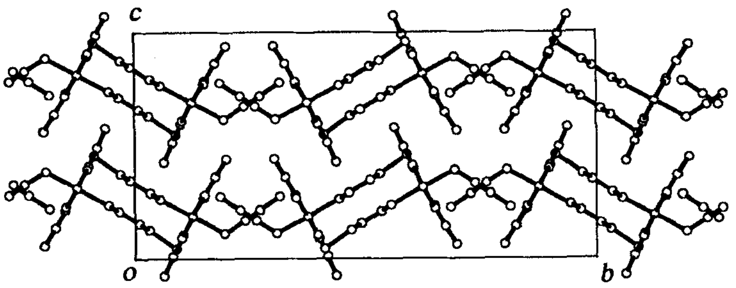


FIGURE 2 Crystal structure of **2** viewed along the *a* axis.

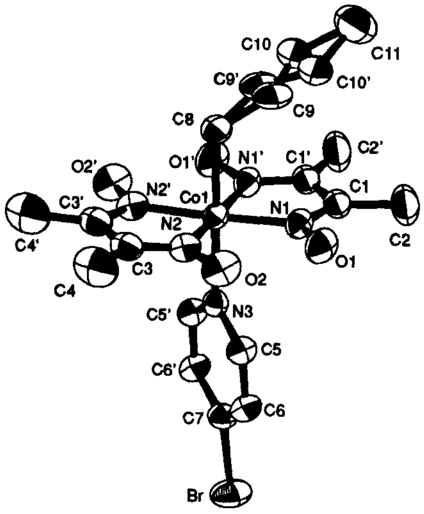


FIGURE 3 Molecular structure of **2**.

The crystal was exposed to a high flux xenon lamp (San-ei SUPER BRIGHT 150) on a 4-circle diffractometer and the cell dimensions were determined. The light was brought to the crystal with a glass fiber tube, the top of which was apart from 17 mm from the crystal. After 19 hours exposure the changes became significantly small and the peak profile of the reflections became broad. The differences before and after the irradiation are 0.006, 0.008, 0.248 Å and 44 $Å^3$ for a, b, c and V, respectively. The irradiation was stopped and the intensity data were collected. The space group remained unaltered. The crystal data are as follows; $C_{17}H_{25}BrCoN_5O_4$, $Mr = 502.26$, orthorhombic, space group *Cmca*, $Z = 8$, $a = 11.887(4)$, $b = 13.291(4)$, $c = 26.707(3)$ Å, $V = 4219(2)$ $Å^3$, $Dx = 1.584$ Mgm^{-3}, $\mu = 2.740$ mm^{-1}. Final $R(F)$ and $wR(F^2)$ values became 0.057 and 0.129, respectively. The crystal structure is essentially the same as that before the irradiation. In order to examine the disordered structure of the 2-butenyl group, the structure viewed along the normal to the cobaloxime plane is shown in FIGURE 4, in which only a half of the disordered structure of the 2-butenyl groups is drawn and their mirror images are omitted for clarity. The *trans*-2-butenyl group, C8-C9A-C10A-C11A, has approximately the same conformation as that before the irradiation. The newly appeared peaks are easily assigned as disordered *cis*-2-butenyl groups, C8-C9B-C10B-C11B. The occupancy factors are 0.26(1), 0.24(2) for A, B 2-butenyl groups, respectively. These results clearly indicate that 48% of *trans*-2-butenyl group isomerizes to its *cis* isomer on exposure to the xenon lamp for about 19 hours.

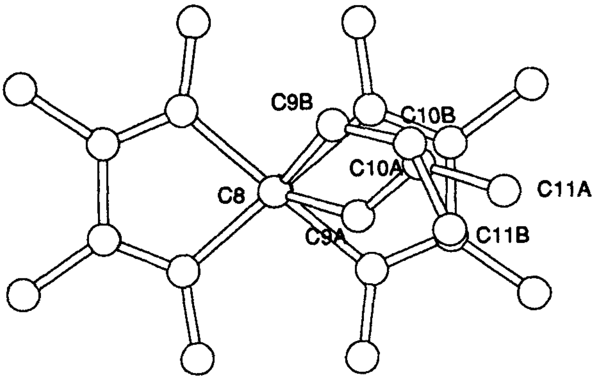


FIGURE 4 Molecular structure of **2** after the irradiation viewed along the normal to the cobaloxime plane.

3-Chloropyridine Complex and Methylsulfide Complex

For the 3-chloropyridine complex the crystal data are as follows; $C_{17}H_{25}ClCoN_5O_4$, $Mr = 457.80$, triclinic, space group $P1$, $Z = 2$, $a = 8.690(2)$, $b = 16.537(6)$, $c = 8.345(3)$ Å, $\alpha = 92.47(3)$, $\beta = 115.69(2)$, $\gamma = 102.05(3)$ °, $V = 1044.5(6)$ Å^3, $Dx = 1.456$ Mgm^{-3}, $\mu = 0.982$ mm^{-1}. The crystal structure is shown in FIGURE 5. Final $R(F)$ and $wR(F^2)$ values became 0.053 and 0.125, respectively. Different from the crystal, a whole molecule is independent in the crystal structure. The molecular structure is given in FIGURE 6, the *trans*-2-butenyl group being disordered as observed in the 4-bromopyridine complex, although it has no longer crystallographic mirror plane. The occupancy factors are 0.63(1) and 0.37(1) for the disordered *trans*-2-butenyl groups, C9-C10A-C11A-C12A and C9-C10B-C11B-C12B, respectively. The unit cell constants and the structure did not change significantly after the irradiation. The similar structure was observed for the methylsulfide complex, although the space groups is $P2_1/n$. This complex is also non-reactive.

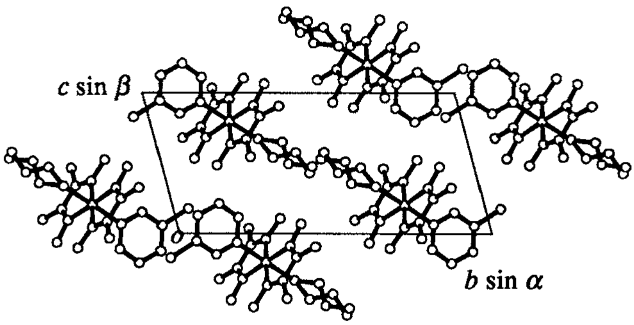


FIGURE 5 Crystal structure of **3** viewed along the *a* axis.

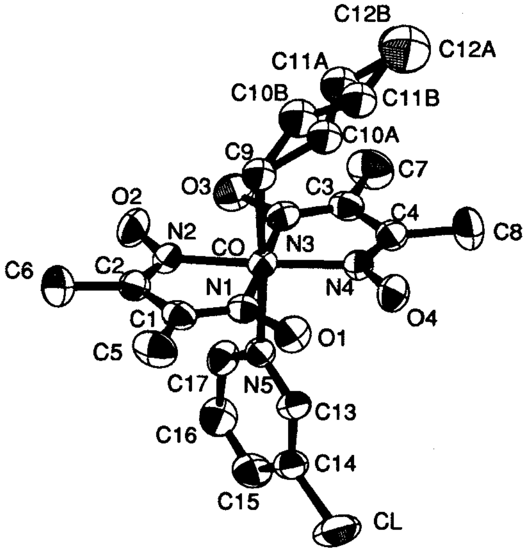
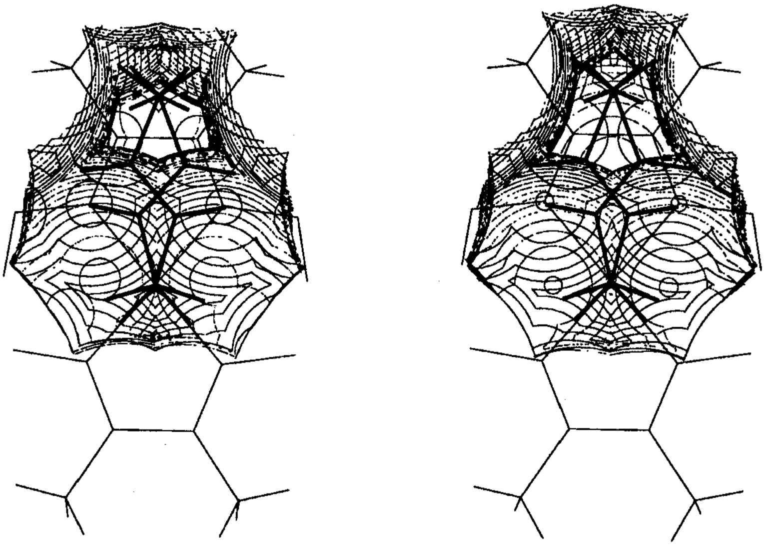


FIGURE 6 Molecular structure of **3**

REACTION CAVITY

Reaction cavity for the 2-butenyl group in each structure before the irradiation was calculated in the same manner as reported previously.[1] FIGURE 7 shows the reaction cavities viewed along the normal to the cobaloxime plane for four complex crystals. The reaction cavities for reactive pyridine and 4-bromopyridine complexes are 17.9 Å^3, 17.1 Å^3, respectively. This may explain the reason why such a large change of the structure can be proceed with retention of the single crystal form. A fairly wide void-

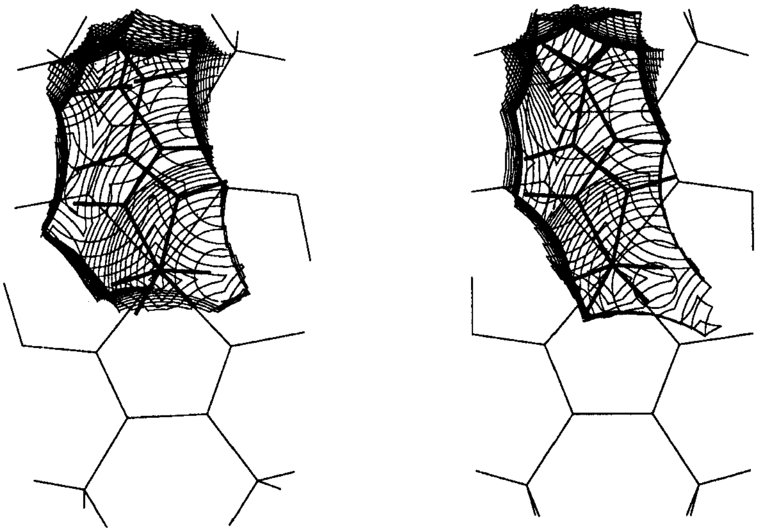
Reactive Complexes



1; 17.9 Å^3

2; 17.1 Å^3

Non-reactive Complexes



3; 17.0 Å^3

4; 14.1 Å^3

FIGURE 7 Reaction cavities for *trans*-2-butenyl complexes.

space is observed in the neighborhood of the *trans*-2-butenyl group of **1** and **2**. The *cis* isomers produced occupy the void space. Since the crystal structure of the 4-bromopyridine complex is similar to that of the pyridine complex before the irradiation, shapes of their reaction cavities are very similar, but the volume is smaller by 0.8 Å^3 than that of the pyridine complex. The smaller cavity of the 4-bromopyridine complex may be responsible to the smaller reaction rate.

As described above, the 3-chloropyridine and methylsulfide complexes showed no reactivity. The volume of the methylsulfide complex is 14.1 Å^3, much smaller than those of reactive pyridine and of 4-bromopyridine complexes. The 3-chloropyridine complex has nearly the same size of cavity as that of the 4-bromopyridine complex. The shape of the cavity of the 3-chloropyridine complex is very similar to that of the methylsulfide complex and there is no room in the cavity to accommodate the *cis* isomer.

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