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ABNORMAL THERMAL EXPANSION AND SOLID-STATE RACEMIZATION OF COBALOXIME COMPLEX CRYSTAL

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The crystals of R-α-cyanoethyl(S-α-methylbenzylamine)cobaloxime exhibit abnormally anisotropic thermal expansion coefficients. The racemization of the cyanoethyl group in the crystalline state by X-ray exposure [Ohashi and Sasada, Nature, 267, 142 (1977)], is no longer observed below 173K. From structure analyses at 173K and room temperature, the mechanism of the racemization has been made clear.

Recently we have found that the crystal of R-α-cyanoethyl(S-α-methylbenzylamine)cobaloxime, cobaloxime being the abbreviation of bis(dimethylglyoximato)-cobalt, changes its unit cell dimensions by X-ray exposure without degradation of a single crystal form, and proved from the electron density calculation that the change reflects the racemization of the cyanoethyl group.$^{1)}$

Since it seemed that the rate of this solid-state reaction depends on the temperature, we made the low temperature experiment on a Rigaku automated four-circle diffractometer. When the crystal was cooled at 133K, the gradual change of its unit cell dimensions by X-ray exposure was no longer detectable. The values of a, b, c and β are 8.791(2), 13.516(2), 9.161(2)Å and 98.31(3)° respectively, their contraction from the values at room temperature being very characteristic. Therefore, the unit cell dimensions were measured at several temperatures.

In Fig.1, the relative values to those at 133K are plotted against temperature. As the temperature is raised, the crystal does "contract" appreciably along the a axis. This is remarkable even if the decrease of β is allowed for. The b value decreases slightly. On the other hand, the value of c increases to an abnormally great extent. At 293K they are 8.665(2), 13.485(3), 9.584(3)Å and 96.95(3)°. In view of experimental error, ther are no discontinuous changes of cell dimensions with temperature. The linear coefficients of thermal expansion were derived to be -1.00×10^{-4}, -0.10×10^{-4} and $2.95\times10^{-4}K^{-1}$ for a, b and c, respectively.

Since the cell dimensions vary with X-ray exposure near the room temperature, it is impossible to examine whether the change with temperature is reversible or not. However, it was confirmed that the thermal expansion of the crystal of the racemate is reversible with the similar expansion coefficients (-1.00×10^{-4}, 0.25×10^{-4} and $2.50\times10^{-4}K^{-1}$ for a, b and c, respectively). Therefore, the thermal expansion behaviour is probably reversible for this crystal.

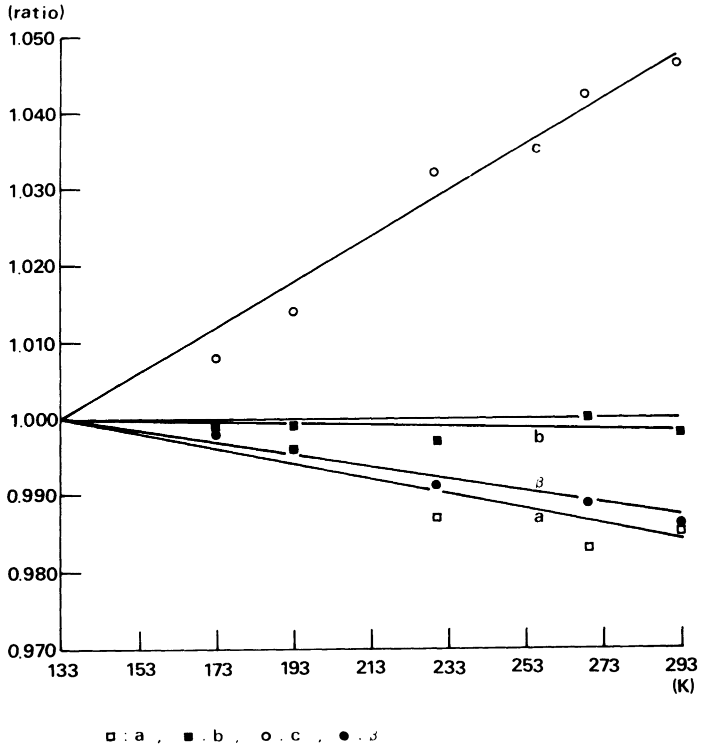

Fig.1 The change of the unit cell dimensions with temperature. Each value is normalized by the corresponding one at 133K. The values of *a* at 173K and 193K are the same as those of *b* and β, respectively. The crystal was cooled by nitrogen gas flow method; the precision of temperature is ±1K. Cell dimensions were determined by least-squares analysis with 9 high-angle reflexions.

These findings should be related to the crystal structure. Refinement of the structures of the present crystal and racemate at 293K was made and both structures at 173K were analyzed. The stereoscopic view of the crystal structure at 293K are shown in Fig.2. The atoms in the vicinity of the α-cyanoethyl group and the short interatomic distances are depicted in Fig.3, where the cyano group makes close contacts with the neighbouring molecule at -x, 1/2+y, 1-z. The N(6) atom forms a weak hydrogen bond with N(5). Between the methyl of the cyanoethyl group and the adjoining molecule along the a axis are the usual van der Waals contacts. On the other hand, the H(17) atom makes very loose contacts with the neighbouring molecule related by 2_1 symmetry, leaving a space around it.

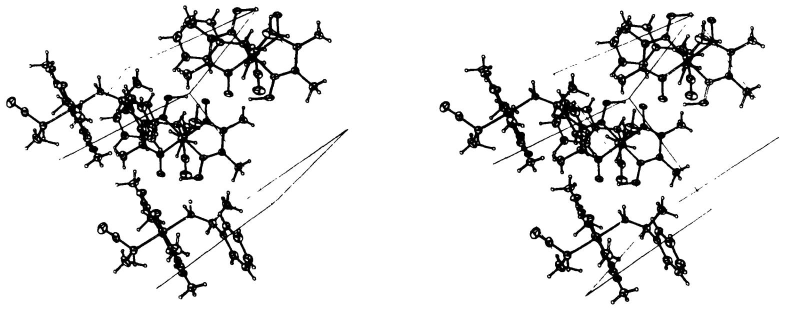

Fig.2 The stereoscopic view of the crystal structure at 293K projected down the axis normal to the average plane of the cobaloxime in the original unit. The thermal ellipsoids are drawn at 20% probability level.

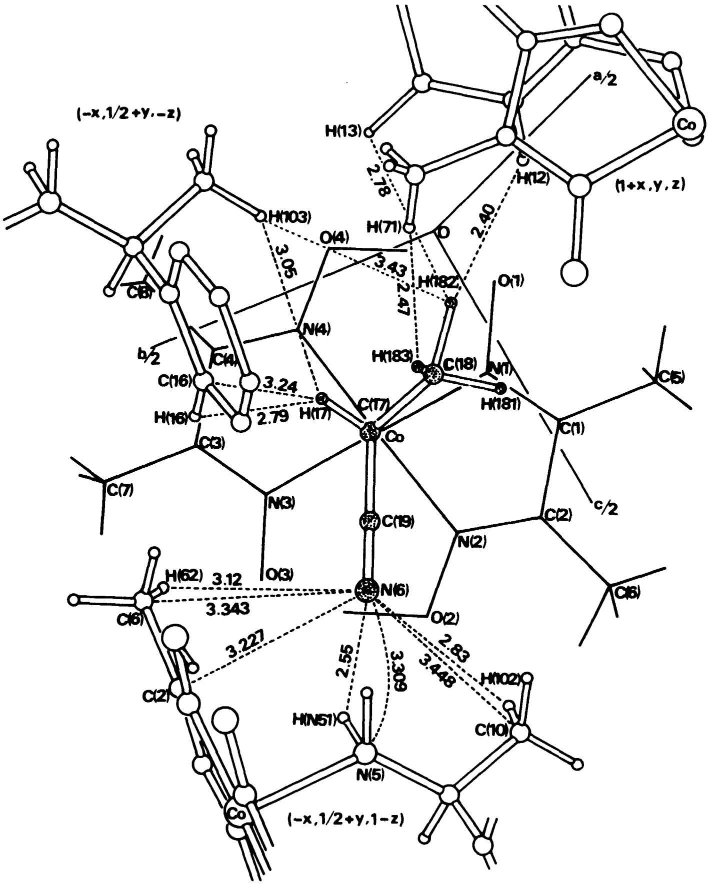

Fig.3 The atoms in the vicinity of the α-cyanoethyl group and the short interatomic distances at 293K. The shadowed atoms are those of the α-cyanoethyl group in the original unit. The space group is $P2_1$. The coordinates of equivalent positions are follows; (1+x, y, z): translation along the a axis,
(-x, 1/2+y, -z): symmetry operation by 2_1 axis and
(-x, 1/2+y, 1-z): symmetry operation by 2_1 axis and translation along the c axis.

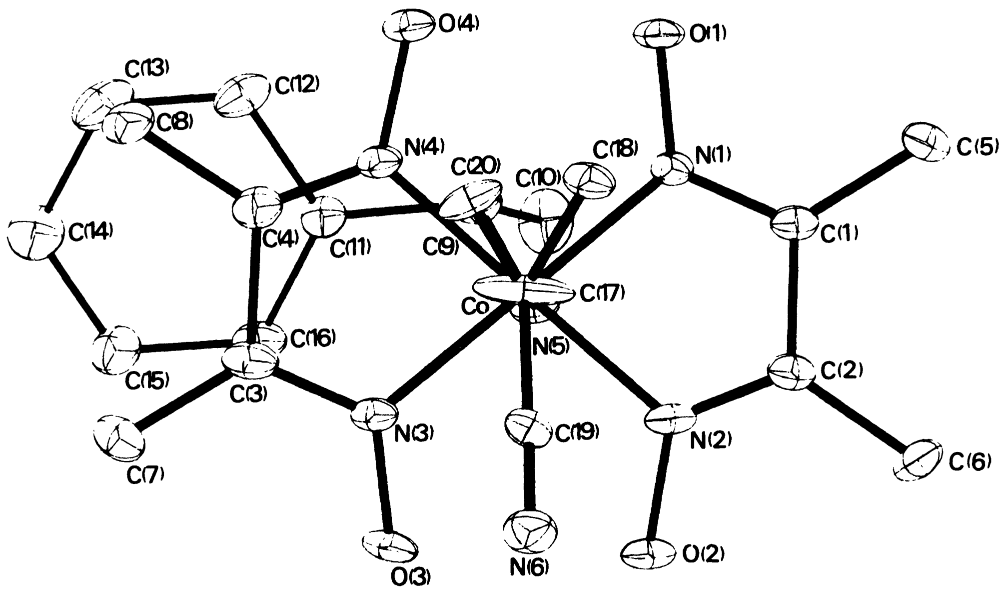

Fig.4 The racemic structure at 173K viewed along the normal to the average plane of the cobaloxime. The thermal ellipsoids are drawn at 30% probability. The hydrogen atoms are omitted for clarity. The abnormally anisotropic thermal motion of C(17) indicates its disordered position.

Table 1 The difference in the interatomic distance between the structures at 173K and 293K. Equivalent positions I, II and III are -x, 1/2+y, -z; 1+x, y, z and -x, 1/2+y, 1-z, respectively.

atom	atom	position	distance(ℓ/Å)	
			173K	293K
C(19)	C(6)	III	3.561(8)	3.664(12)
C(19)	H(62)	III	2.56(7)	3.28(7)
N(6)	C(2)	III	3.242(8)	3.227(11)
N(6)	C(6)	III	3.386(8)	3.343(12)
N(6)	H(62)	III	2.57(7)	3.12(7)
N(6)	N(5)	III	3.218(7)	3.309(10)
N(6)	H(N51)	III	2.34(5)	2.55(7)
N(6)	C(10)	III	3.438(8)	3.448(12)
N(6)	H(102)	III	2.76(6)	2.83(7)
H(182)	H(12)	II	2.97(7)	2.40(12)
H(182)	H(13)	II	2.85(9)	2.78(13)
H(183)	H(71)	II	2.54(7)	2.47(11)
H(17)	H(103)	I	2.47(8)	3.05(10)
H(17)	H(16)	I	2.53(9)	3.24(8)
H(182)	H(103)	I	2.56(8)	3.43(12)

As suggested in the previous paper,[1] the planar cyanoethyl radical produced by the Co-C bond cleavage may rotate around the C-C≡N axis to face the opposite side of the plane to the cobalt atom and recombine with the cobalt to give the racemic crystal. Figure 4 shows the racemic structure, which is produced by X-ray exposure at room temperature. The methyl group of S configuration, C(20), fills up the space around H(17). However, the space is so small for the methyl group that the value of *b* would increase as the racemates grow.

When the crystal is cooled, it contracts to a great extent along the c axis and the space around H(17) is filled up. The interatomic distances at 173K are listed in Table 1. The distances, H(17)...H(103), H(17)...H(16) and H(182)...H(103) are 2.47, 2.53 and 2.56Å respectively, which are usual van der Waals contacts. These structural features well explain the inhibition of the racemization.

The conformations around the Co-C(17), Co-N(5) and N(5)-C(9) bonds are not so different between the structures at 173K and 293K. The angles of C(19)-C(17)-Co-N(2), N(4)-Co-N(5)-C(9) and Co-N(5)-C(9)-C(10) are 37.4°, 19.8° and 159.5°, respectively for 173K, whereas 37.2°, 23.2° and 159.1° for 293K. A slight decrease in N(4)-Co-N(5)-C(9) angle at low temperature contributes, although to a small extent, the close packing around H(17).

Reference

1) Y. Ohashi and Y. Sasada, Nature, 267, 142 (1977).

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