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Crystalline-State Reaction of Cobaloxime Complexes. 16.*
Two Polymorphs of [(S)-1-Cyanoethyl][(S)-phenylethylamine]cobaloxime

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Abstract

Two polymorphs were found for the title complex. One is racemized without degradation of the crystallinity on exposure to visible light as well as X-rays, whereas the other, which has two solvent molecules in an asymmetric unit, is non-reactive. The different reactivities of two crystal forms can be well explained by the size of the reaction cavity for the chiral 1-cyanoethyl group. The rates of the racemization were measured and the crystal structures were determined at four different temperatures, 223, 253, 296 and 333 K. A good correlation was obtained between the rate constant and the reaction cavity in the range of these temperatures.

Introduction

Since it was found that the chiral 1-cyanoethyl (ce) group bonded to the cobalt atom in the crystal of [(R)-1-cyanoethyl][(S)-phenylethylamine]bis(2,3-

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* Part 15: Osano, Danno, Uchida, Ohashi, Ohgo & Baba (1991).
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butanedione dioximato)cobalt(III), *R-S*-pea cobaloxime complex, is racemized by X-ray exposure without degradation of the single-crystal form (Ohashi & Sasada, 1977; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), some related crystals with various amines or phosphines as axial base ligands have been shown to undergo crystalline-state racemization (Ohashi, 1988). The reaction can be followed by the change in lattice parameters and often proceeds slowly enough to allow the crystal structure analysis to be made at the initial, intermediate and final stages. The change in parameters with exposure time follows first-order kinetics. In order to explain the mode and rate of the crystalline-state racemization, the reaction cavity, the void space around the reactive group, was defined (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981). A good correlation between the reaction rate and the volume of the reaction cavity has been obtained (Takenaka, Ohashi, Tamura, Uchida, Sasada, Ohgo & Baba, 1993).

Recently, the complex of [(S)-1-cyanoethyl][(S)-phenylethylamine]cobaloxime, *S-S*-pea, which is a diastereoisomer of *R-S*-pea, was found to have two

Table 1. *Crystallographic data and experimental conditions*

| | *S-S*-pea(I) | | | | | *S-S*-pea(II) | |
| | Initial | | | | Final | | |
	223 K	253 K	296 K	333 K	296 K	223 K	296 K
a (Å)	8.712 (5)	8.746 (5)	8.777 (2)	8.818 (2)	8.818 (6)	16.783 (5)	16.938 (6)
b (Å)	13.306 (7)	13.332 (6)	13.390 (3)	13.426 (3)	13.713 (6)	10.739 (3)	10.758 (4)
c (Å)	9.531 (6)	9.538 (3)	9.540 (2)	9.553 (2)	9.419 (5)	6.826 (4)	6.848 (5)
β (°)	96.51 (5)	96.60 (3)	96.79 (3)	96.93 (2)	98.80 (8)	99.76 (4)	99.84 (5)
V (Å^3)	1097.7 (9)	1104.8 (7)	1113.3 (4)	1122.8 (4)	1126 (1)	1212.5 (9)	1230 (1)
D_x (Mg m^{-3})	1.41	1.40	1.39	1.37	1.37	1.37	1.35
μ (mm^{-1})	0.814	0.809	0.802	0.796	0.794	0.747	0.737
Crystal size (mm)	0.4	0.4	0.5	0.5	0.45	0.4	0.5
	0.4	0.3	0.4	0.3	0.4	0.35	0.4
	0.2	0.2	0.2	0.3	0.2	0.15	0.2
$\sin\theta/\lambda_{max}$ (Å^{-1})	0.65	0.59	0.65	0.65	0.65	0.59	0.65
h_{min}	0	0	0	0	-13	0	0
h_{max}	11	10	11	11	13	20	22
k_{min}	0	0	0	0	0	0	0
k_{max}	17	16	17	17	18	13	14
l_{min}	-12	-11	-12	-12	0	-8	-9
l_{max}	12	11	12	12	14	8	9
No. of reflections measured	2645	2050	2678	2635	2697	2336	2900
No. of reflections used	2424	1656	1887	1886	2438	1648	2183
No. of parameters	386	386	270	270	315	288	288
R	0.030	0.033	0.045	0.060	0.052	0.050	0.041
wR	0.036	0.034	0.041	0.070	0.051	0.053	0.047
S	1.45	1.29	1.38	2.32	1.19	1.71	1.71
$(\Delta/\sigma)_{max}$	0.04	0.05	0.09	0.11	0.28	0.05	0.03
$\Delta\rho_{max}$ (e Å^{-3})	0.46	0.33	0.45	0.57	0.82	0.63	0.40

crystal forms, *S-S*-pea(I) and *S-S*-pea(II), when it was crystallized in an aqueous methanol solution. The *S-S*-pea(I) crystal showed the crystalline-state racemization whereas *S-S*-pea(II) was non-reactive on exposure to visible light or X-rays. The recent work was undertaken to explain why the two crystals have different reactivity and to analyze the temperature dependence of the reaction rate more quantitatively for the reactive *S-S*-pea(I).

Experimental

The title compound was prepared as reported previously (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981). Two forms of crystals were obtained from an aqueous methanol solution in the same batch; *S-S*-pea(I) is platelike and *S-S*-pea(II) is needlelike. *S-S*-pea(I) is stable under normal atmospheric conditions but *S-S*-pea(II) is unstable at room temperature. Moreover, *S-S*-pea(I) was revealed to be racemized without degradation of the single-crystal form and was identified as the crystal whose structure had been determined previously (Ohashi, Sasada & Ohgo, 1978; Ohashi, Sasada, Takeuchi & Ohgo, 1980).

The change of cell dimensions with exposure time was measured for *S-S*-pea(I) at four different temperatures (223, 253, 296 and 333 K) on a Rigaku AFC-5 four-circle diffractometer with Mo $K\alpha$ radiation monochromated by graphite (55 kV, 150 mA, λ = 0.7107 Å) using a nitrogen gas-flow method. It was found that the crystal racemized much faster by irradiation with a Xe lamp than on exposure to X-rays. Therefore, the crystal mounted on the dif-

fractometer was exposed to visible light (obtained from a Xe lamp *via* a glass fibre tube) throughout the measurement. The determination of cell dimensions was repeated continuously using 25 2θ values in the range 20 < 2θ < 30°. The parameters for *S-S*-pea(II) were also determined at two temperatures (223 and 296 K) using 25 2θ values. The change in cell parameters was not observed for *S-S*-pea(II).

Three-dimensional intensity data were collected at the initial and the final stages for *S-S*-pea(I). The Xe lamp was turned off during the measurement. Before and after the data collection, cell parameters were determined as mentioned in the previous paragraph and the average values were used for the structure analysis. These values are listed in Table 1. Intensity data were collected by means of an ω–2θ scan technique at 32° min^{-1} in 2θ at 223, 253, 296 and 333 K at the initial stage with an AFC-5 diffractometer, and at 4° min^{-1} using a Rigaku AFC-4 four-circle diffractometer with Mo $K\alpha$ radiation (45 kV, 20 mA) at 296 K at the final stage. The space group did not change in the process of the reaction. The structure factors of three monitor reflexions did not vary significantly at each stage. Reflexions with $|F|$ $\geq 3\sigma(F)$ were used for the structure determination. Crystal data: $C_{19}H_{29}N_6O_4Co$, $M_r = 464.4$, monoclinic, $P2_1$, $Z = 2$, $F(000) = 488$; the other data and experimental details are listed in Table 1.

For *S-S*-pea(II), the crystal was sealed in a glass capillary during the data collection at 296 K. Crystal data: $C_{19}H_{29}N_6O_4Co.2H_2O$, $M_r = 500.4$, monoclinic, $P2_1$, $Z = 2$, $F(000) = 528$. The scan speed at 223 K was 16° min^{-1} in 2θ using the AFC-5 diffractometer. The other conditions are the same as those of *S-S*-pea(I).

Table 2. *Redetermined atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non-H atoms of S-S-pea*(I) *at* 296 K

Original parameters were reported by Ohashi *et al.* (1980).

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	-0.0119 (1)	0.7496	0.73518 (7)	2.53 (3)
O(1)	0.2465 (5)	0.6413 (5)	0.6649 (5)	4.2 (2)
O(2)	-0.1303 (5)	0.7584 (6)	1.0014 (4)	4.2 (2)
O(3)	-0.2598 (5)	0.8671 (4)	0.8126 (4)	3.9 (2)
O(4)	0.1114 (5)	0.7462 (6)	0.4723 (4)	4.2 (2)
N(1)	0.1554 (7)	0.6612 (5)	0.7633 (6)	3.1 (3)
N(2)	-0.0251 (7)	0.7163 (4)	0.9254 (5)	3.1 (2)
N(3)	-0.1787 (7)	0.8383 (5)	0.7073 (6)	2.9 (3)
N(4)	-0.0007 (6)	0.7814 (4)	0.5445 (5)	3.1 (3)
N(5)	-0.0814 (9)	0.5424 (5)	0.4559 (7)	5.9 (4)
N(6)	0.1178 (6)	0.8743 (5)	0.7934 (6)	3.0 (3)
C(1)	0.1804 (8)	0.6188 (6)	0.8874 (7)	3.3 (3)
C(2)	0.0732 (8)	0.6531 (6)	0.9841 (6)	3.3 (3)
C(3)	-0.2085 (7)	0.8769 (6)	0.5822 (7)	3.1 (3)
C(4)	-0.1064 (8)	0.8410 (6)	0.4854 (6)	3.3 (3)
C(5)	0.308 (1)	0.5477 (6)	0.9270 (8)	4.8 (4)
C(6)	0.079 (1)	0.6191 (7)	1.1335 (7)	5.2 (4)
C(7)	-0.3323 (9)	0.9522 (7)	0.5429 (8)	4.8 (4)
C(8)	-0.1156 (9)	0.8704 (7)	0.3321 (7)	4.5 (3)
C(9)	-0.151 (1)	0.6289 (6)	0.6818 (8)	3.8 (4)
C(10)	-0.319 (1)	0.6411 (9)	0.680 (1)	7.8 (6)
C(11)	-0.1106 (8)	0.5811 (6)	0.5544 (7)	4.1 (3)
C(12)	0.2880 (8)	0.8741 (6)	0.8326 (7)	3.5 (3)
C(13)	0.354 (1)	0.9791 (7)	0.8126 (8)	5.8 (4)
C(14)	0.3352 (7)	0.8412 (5)	0.9837 (7)	3.4 (3)
C(15)	0.4640 (7)	0.7827 (6)	1.0108 (8)	4.5 (3)
C(16)	0.5179 (9)	0.7555 (9)	1.149 (1)	6.4 (4)
C(17)	0.440 (1)	0.7867 (7)	1.258 (1)	6.6 (5)
C(18)	0.312 (1)	0.8468 (8)	1.2301 (8)	6.1 (4)
C(19)	0.2598 (8)	0.8725 (7)	1.0958 (7)	4.9 (4)

Table 3. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non-H atoms of S-S-pea*(I) *at* 296 K *at the final stage*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	-0.01539 (7)	0.7496	0.73143 (6)	3.31 (1)
O(1)	0.2389 (5)	0.6420 (3)	0.6657 (4)	5.1 (1)
O(2)	-0.1331 (4)	0.7588 (5)	0.9972 (3)	5.3 (1)
O(3)	-0.2611 (4)	0.8659 (3)	0.8040 (4)	4.9 (1)
O(4)	0.1081 (4)	0.7480 (5)	0.4692 (3)	5.11 (9)
N(1)	0.1484 (6)	0.6609 (4)	0.7641 (5)	4.2 (1)
N(2)	-0.0301 (5)	0.7156 (4)	0.9236 (4)	4.1 (1)
N(3)	-0.1774 (5)	0.8393 (4)	0.6998 (5)	3.5 (1)
N(4)	-0.0030 (5)	0.7816 (3)	0.5400 (4)	3.9 (1)
N(5)	-0.0809 (8)	0.5428 (5)	0.4527 (6)	6.9 (1)
N(6)	0.1212 (5)	0.8691 (3)	0.7946 (5)	3.6 (1)
C(1)	0.1742 (7)	0.6180 (4)	0.8896 (6)	4.4 (1)
C(2)	0.0659 (7)	0.6533 (5)	0.9851 (6)	4.3 (1)
C(3)	-0.2073 (6)	0.8783 (5)	0.5732 (6)	4.2 (1)
C(4)	-0.1028 (6)	0.8441 (5)	0.4777 (5)	4.1 (1)
C(5)	0.2995 (7)	0.5475 (5)	0.9373 (7)	5.8 (1)
C(6)	0.0683 (9)	0.6183 (6)	1.1350 (7)	6.6 (2)
C(7)	-0.3300 (7)	0.9529 (6)	0.5330 (7)	5.9 (1)
C(8)	-0.1116 (8)	0.8756 (6)	0.3256 (6)	6.1 (1)
C(9)	-0.165 (1)	0.6391 (6)	0.6622 (9)	6.7 (2)
C(10S)†	-0.325 (2)	0.641 (1)	0.672 (2)	6.8 (2)
C(10R)†	-0.244 (2)	0.587 (1)	0.755 (2)	6.8 (2)
C(11)	-0.1165 (7)	0.5859 (5)	0.5447 (6)	5.1 (1)
C(12)	0.2923 (6)	0.8671 (5)	0.8326 (6)	4.2 (1)
C(13)	0.3595 (7)	0.9643 (5)	0.8161 (7)	5.8 (1)
C(14)	0.3433 (6)	0.8284 (4)	0.9843 (6)	4.2 (1)
C(15)	0.4757 (7)	0.7742 (5)	1.0087 (8)	5.9 (1)
C(16)	0.5348 (8)	0.7430 (7)	1.1488 (9)	7.9 (2)
C(17)	0.460 (1)	0.7675 (9)	1.2604 (8)	9.7 (2)
C(18)	0.3297 (8)	0.8216 (8)	1.2358 (8)	8.8 (2)
C(19)	0.2740 (7)	0.8518 (7)	1.1000 (7)	6.6 (1)

† Occupancy factors for C(10S) and C(10R) are 0.5.

Structure determination

Structure determination was carried out by the *TEXSAN* system (Molecular Structure Corporation, 1985). Structures of S-S-pea(I) at the initial stages at four different temperatures were refined by full-matrix least squares based on F with $w = [\sigma^2(|F_o|) + a|F_o|^2]^{-1}$, where $a = 0.017$, 0.014, 0.015 and 0.015 for 223, 253, 296 and 333 K, respectively. Anisotropic thermal parameters were applied to non-H atoms. H atoms were located by calculations assuming a C—H distance of 1.00 Å and refined isotropically at 223 and 253 K or fixed by the geometric calculations at 296 and 333 K. Other refinement details are also listed in Table 1. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) including the anomalous-dispersion terms. No absorption and extinction corrections were applied. The atomic parameters for non-H atoms at 296 K are given in Table 2.*

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* Lists of structure factors, positional and thermal parameters for non-H atoms at 223, 253 and 333 K for S-S-pea(I) and at 223 K for S-S-pea(II), anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71063 (121 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0632]

The structure of S-S-pea(I) at the final stage was refined by full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976), based on F with $w = [\sigma^2(|F_o|) + 0.0005|F_o|^2]^{-1}$ using the parameters of the initial structure. The peak corresponding to the methyl of the R-ce group was found on the difference map and then C(10) was treated as a disordered structure. Site occupancies of C(10S) and C(10R) were converged to 0.5 within the standard deviation and therefore were fixed to 0.5. The non-H atoms were refined anisotropically except that C(10S) and C(10R) were refined isotropically with the same thermal parameter. H atoms bonded to O(2) and O(4) atoms were refined isotropically, those bonded to C(9) were not included, methyl groups were treated as rigid groups, and the other H atoms were refined isotropically riding on the bonding atoms. Other refinement details are listed in Table 1 and the atomic parameters for non-H atoms in Table 3.

The structure of S-S-pea(II) was solved by direct methods and refined by full-matrix least squares based on F with $w = (\sigma^2|F_o| + a|F_o|^2)^{-1}$, where $a = 0.015$ and 0.017 for 223 and 296 K, respectively. Anisotropic thermal parameters were applied to non-H atoms. H atoms were fixed by the geometric calculations. The atomic parameters for non-H atoms at 296 K are given in Table 4.

Table 4. *Atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$) *for non-H atoms of S-S-pea*(II) *at* 296 K

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	0.70089 (4)	0.2706	0.3437 (1)	2.49 (2)
O(1)	0.7804 (3)	0.2364 (4)	0.7438 (6)	4.4 (2)
O(2)	0.7037 (3)	0.4810 (4)	0.0995 (6)	4.4 (2)
O(3)	0.6103 (2)	0.3104 (4)	−0.0452 (6)	3.7 (2)
O(4)	0.7006 (3)	0.0578 (4)	0.5886 (6)	4.8 (2)
O(5)	0.2452 (3)	0.4489 (5)	0.0372 (7)	6.2 (3)
O(6)	0.3083 (4)	0.2120 (5)	0.085 (1)	8.8 (3)
N(1)	0.7673 (3)	0.3126 (4)	0.5842 (6)	2.9 (2)
N(2)	0.7315 (3)	0.4320 (5)	0.2746 (7)	3.1 (2)
N(3)	0.6331 (3)	0.2284 (5)	0.1081 (7)	3.1 (2)
N(4)	0.6710 (3)	0.1077 (5)	0.4104 (7)	3.3 (2)
N(5)	0.4721 (3)	0.2528 (7)	0.2963 (9)	5.1 (3)
N(6)	0.7935 (3)	0.2002 (4)	0.2113 (7)	2.9 (2)
C(1)	0.8031 (3)	0.4198 (6)	0.5942 (9)	3.3 (2)
C(2)	0.7812 (4)	0.4907 (6)	0.407 (1)	3.6 (3)
C(3)	0.6021 (3)	0.1178 (6)	0.0932 (9)	3.2 (3)
C(4)	0.6279 (4)	0.0448 (6)	0.272 (1)	3.2 (3)
C(5)	0.8559 (4)	0.4663 (8)	0.775 (1)	5.3 (4)
C(6)	0.8118 (6)	0.6182 (9)	0.377 (1)	7.0 (5)
C(7)	0.5458 (4)	0.0725 (8)	−0.085 (1)	4.8 (3)
C(8)	0.6048 (5)	−0.0879 (7)	0.293 (1)	5.1 (4)
C(9)	0.6096 (4)	0.3331 (6)	0.4768 (9)	3.4 (3)
C(10)	0.6046 (4)	0.4739 (7)	0.515 (1)	4.8 (3)
C(11)	0.5319 (3)	0.2880 (8)	0.3753 (8)	3.3 (3)
C(12)	0.8762 (4)	0.1782 (6)	0.3243 (9)	3.7 (3)
C(13)	0.8813 (4)	0.0455 (8)	0.402 (1)	5.5 (4)
C(14)	0.9403 (4)	0.2075 (6)	0.206 (1)	3.6 (3)
C(15)	0.9992 (4)	0.2913 (7)	0.274 (1)	4.8 (3)
C(16)	1.0614 (5)	0.3171 (7)	0.171 (1)	5.9 (4)
C(17)	1.0628 (4)	0.261 (1)	−0.007 (1)	5.2 (3)
C(18)	1.0036 (4)	0.1773 (8)	−0.081 (1)	4.9 (3)
C(19)	0.9434 (4)	0.1485 (7)	0.024 (1)	4.1 (3)

Discussion

Molecular and crystal structure

The characteristics of the crystal and molecular structures of the S-S-pea(I) complex were discussed previously (Ohashi, Sasada & Ohgo, 1978; Ohashi, Sasada, Takeuchi & Ohgo, 1980).

The molecular structure of S-S-pea(II) at 296 K and the numbering of the atoms is shown in Fig. 1.

The crystal structure of S-S-pea(II) viewed along the b axis is shown in Fig. 2. The structure of S-S-pea(I) is also shown for comparison. The two structures are very different from each other. There are one S-S-pea(II) molecule and two solvent water molecules in an asymmetric unit of S-S-pea(II). The N atom in the ce group is connected to a water molecule by a hydrogen bond [N(5)···O(6) = 2.935 (8) Å at 296 K]. A similar hydrogen bond was observed in the related cobaloxime complex crystals which have triphenylphosphine (Kurihara, Uchida, Ohashi, Sasada, Ohgo & Baba, 1983) and pyrrolidine (Takenaka, Ohashi, Tamura, Uchida, Sasada, Ohgo & Baba, 1993) as axial base ligands. Hydrogen bonds N(5)···O(6), O(6)···O(5) [2.761 (8) Å] and O(5)···O(4) [2.825 (7) Å] in S-S-pea(II) make a spiral structure along the twofold screw axis, and O(4)···O(5), O(5)···O(6) and O(6)···O(2) [2.780 (7) Å] make a ribbon along the c axis. The S-S-pea(II) crystal is

unstable presumably because the solvent water molecules are lost at room temperature.

Selected bond distances, bond angles and torsion angles are listed in Table 5. Fig. 3 shows the conformation of the ce group of S-S-pea(I) projected onto the cobaloxime plane at the initial and final stages and the corresponding one of S-S-pea(II) at 296 K. Some atoms of pea are omitted for clarity. The cyano and methyl groups are located over the gaps between two 2,3-butanedione dioximato moieties in the S-S-pea(I) complex. Such a conformation of the ce group is also found in the diastereoisomeric complex of R-S-pea, although the locations of the methyl and cyano groups are exchanged because of the opposite configuration at the C(9) atom. The cyano group in the ce group of the S-S-pea(II) complex, on the other hand, is along the direction bisecting one of the 2,3-butanedione dioximato moieties. The N atom in the ce group of the S-S-pea(I) complex makes a hydrogen bond, although weak, with the H atom bonded to the N(6) atom in the neighbouring molecule [N(5)···N(6) = 3.263 (9) Å at 296 K]. That of S-S-pea(II) is, however, bound to the water solvent as mentioned before.

Reaction cavity

It has been proposed that the packing around the ce group plays an important role in determining the
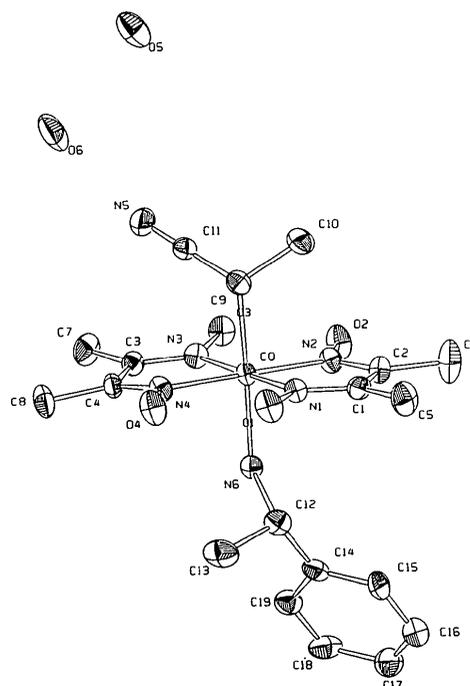
Fig. 1. Molecular structure of S-S-pea(II) at 296 K with the numbering of atoms. The thermal ellipsoids are at 30% probability level.

reactivity and the reaction rate in crystalline-state racemization. The concept of the reaction cavity was defined to visualize the environment in the vicinity of the ce group (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981). The volume of the reaction cavity is a useful index because it concentrates the three-dimensional information of the void space around the reactive group into a one-dimensional parameter.

The cell parameters of S-S-pea(I) were changed with exposure time at each temperature, but those of S-S-pea(II) were not changed even at room temperature. In order to explain this different reactivity, the reaction cavities for S-S-pea(I) and S-S-pea(II) at room temperature are drawn in Fig. 4. The ce group of S-S-pea(II) is closely packed by the surrounding atoms and it seems difficult to invert. The size of the

(a)

(b)

Fig. 2. Crystal structures. Dashed lines indicate hydrogen bonds. (a) S-S-pea(II) at 296 K viewed along b axis; (b) S-S-pea(I) at 296 K viewed along c axis.

(a)

(b)

(c)
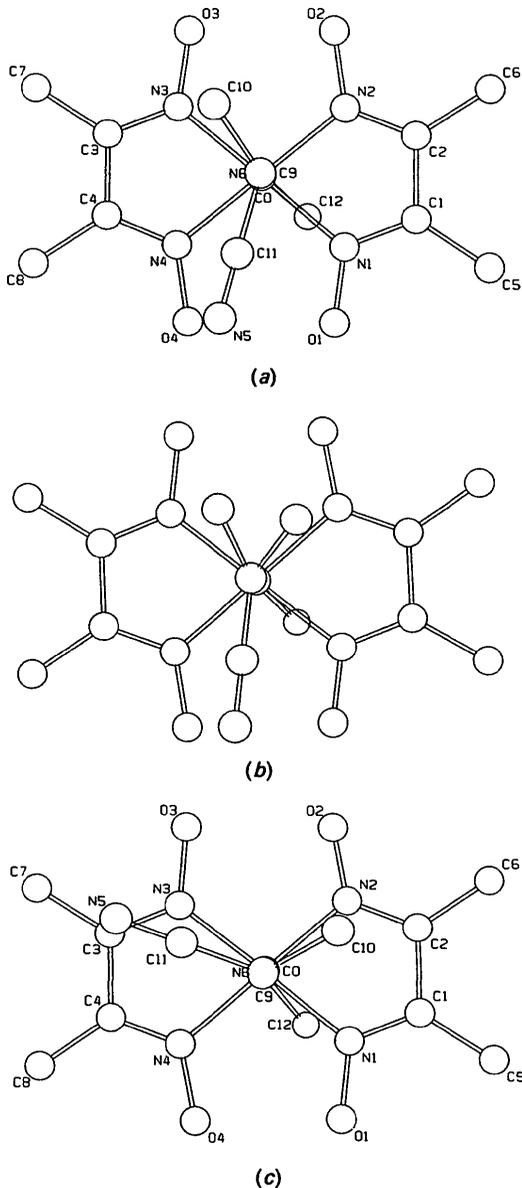
Fig. 3. Conformation of the ce group projected onto the cobaloxime plane. (a) Initial stage of the reaction for S-S-pea(I) at 296 K; (b) final stage of the reaction for S-S-pea(I) at 296 K; (c) S-S-pea(II) at 296 K.

Table 5. *Selected bond distances (Å), bond angles (°) and torsion angles (°)*

	S-S-pea(I) Initial				Final	S-S-pea(II)	
	223 K	253 K	296 K	333 K	296 K	223 K	296 K
Co—C(9)	2.049 (4)	2.056 (8)	2.052 (8)	2.06 (1)	2.050 (8)	2.06 (1)	2.038 (6)
Co—N(6)	2.065 (3)	2.063 (6)	2.059 (6)	2.057 (9)	2.066 (5)	2.077 (8)	2.083 (5)
C(9)—C(10S)	1.519 (7)	1.51 (1)	1.48 (1)	1.51 (2)	1.43 (2)	1.53 (1)	1.543 (9)
C(9)—C(10R)					1.39 (2)		
N(6)—C(12)	1.478 (5)	1.478 (8)	1.497 (8)	1.47 (1)	1.497 (7)	1.51 (1)	1.499 (7)
Co—C(9)—C(10S)	117.0 (3)	116.9 (6)	118.5 (7)	117.2 (9)	124.1 (8)	117.9 (8)	117.9 (5)
Co—C(9)—C(10R)					122.4 (8)		
Co—N(6)—C(12)	125.4 (3)	125.7 (5)	124.7 (5)	126.1 (8)	125.2 (4)	121.9 (5)	122.6 (4)
N(4)—Co—C(9)—C(11)	33.6 (3)	33.5 (5)	34.7 (6)	34 (1)	42.6 (5)	−64.8 (8)	−62.8 (5)
N(3)—Co—C(9)—C(10S)	−14.2 (4)	−14.4 (6)	−16.0 (8)	−18 (1)	−27.3 (9)	−109.7 (8)	−110.6 (5)
N(3)—Co—C(9)—C(10R)					−90.0 (9)		
N(2)—Co—C(9)—C(10S)	84.2 (4)	84.4 (6)	82.5 (8)	81 (1)	71.5 (9)	−11.1 (8)	−11.0 (5)
N(2)—Co—C(9)—C(10R)					8.8 (9)		
N(1)—Co—N(6)—C(12)	1.2 (3)	2.5 (5)	2.8 (5)	1.0 (8)	5.6 (5)	10.1 (7)	10.2 (5)

reaction cavity of S-S-pea(II) was calculated to be 7.7 and 8.6 Å³ at 223 and 296 K, respectively. Those of S-S-pea(I) were 11.6, 11.7, 12.8 and 13.9 Å³ at 223, 253, 296 and 333 K at the initial stage and 14.8 Å³ at the final stage at 296 K. Both S-S-pea(I) and S-S-pea(II) have one independent molecule in an asymmetric unit, which belongs, therefore, to mode I if crystalline-state racemization occurs (Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1985). It was proposed that the threshold of the size of the reaction cavity required to carry out the crystalline-state racemization in mode I is 11.5 Å³ (Takenaka, Ohashi, Tamura, Uchida, Sasada, Ohgo & Baba, 1993). The cavity of S-S-pea(II) is too small to undergo crystalline-state racemization. The size of the cavity of S-S-pea(I), on the other hand, fulfills this condition even at 223 K. Although a hydrogen bond between the N atom in the ce group and the solvent O atom plays an important role in the β–α photoisomerization of the 2-ce group (Sekine & Ohashi, 1991), the corresponding hydrogen bond of S-S-pea(II) seems to have no effect on the racemization of the 1-ce group. This result coincides with the case of [(R)-1-cyanoethyl](pyrrolidine)cobaloxime (Takenaka, Ohashi, Tamura, Uchida, Sasada, Ohgo & Baba, 1993). The different reactivities of these two S-S-pea crystals are explained well by the size of the reaction cavity.

Reaction rate

The cell constants of S-S-pea(I) are changed with the progress of the racemization at 296 K as shown in Fig. 5. Similar features were also observed at other temperatures. The changes are quite anisotropic, the values of a, b, β and the volume increase whereas that of c decreases.

Fig. 5 shows that the change in the unit-cell dimensions follows approximately first-order kinetics as observed in the diastereoisomeric crystal of R-S-pea and other related cobaloxime crystals. For the present crystal, the changes in the cell parameters

b, β and volume are significant with respect to five variables. The rate constants were determined from the change of these three values by least-squares fitting procedures, which are listed in Table 6 with various parameters. The change of cell dimensions was also measured under the condition that the crystal was not exposed to the Xe lamp. The rate constants are also listed in Table 6. It can be seen

(a)

(b)

(c)
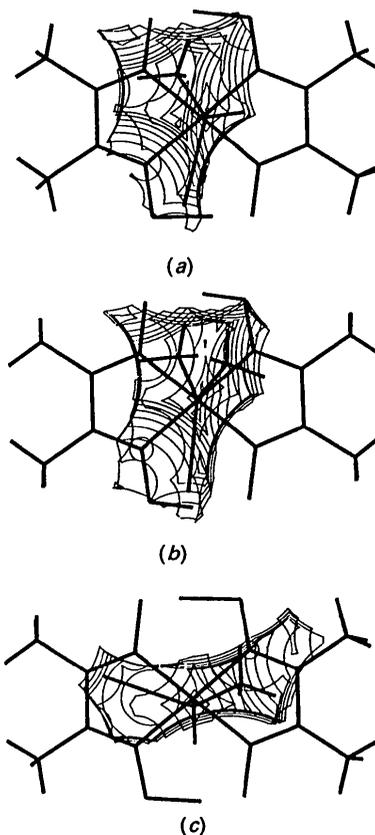
Fig. 4. Reaction cavity projected onto the cobaloxime plane. Contours are drawn in sections separated by 0.2 Å. (a) S-S-pea(I) at the initial stage at 296 K; (b) S-S-pea(I) at the final stage at 296 K; (c) S-S-pea(II) at 296 K.

that the rate constants based on exposure to the Xe lamp are much faster than the corresponding ones for X-ray exposure. The crystalline-state racemization can be accelerated by high-intensity visible light.

Fig. 6 shows the temperature dependence of the reaction rate and the cavity size. The volume of the reaction cavity gradually expands as the temperature increases. The reaction rate determined from the change in cell parameters for the S-S-pea(I) complex is linearly dependent on the size of the cavity. It is clear that the approximately linear relationship between the cavity size and the reaction rate holds good even if the temperature is varied.

Fig. 7 shows an Arrhenius plot for S-S-pea(I). Four points lie approximately on a straight line. The activation energy was estimated to be 9.8 kJ mol^{-1} by a least-squares fitting procedure.

Table 6. *Size of the reaction cavity* (V_{cav}) *and rate constants* (k) *for* S-S-pea(I) *at* 223, 253, 296 *and* 333 K *with crystal size used and lattice constants*

i initial and f final stage of the reaction.

		223 K	253 K	296 K	333 K
Crystal size		40	34	22	26
($\times 10^{-2}$ mm)		30	26	22	18
		14	12	12	10
a (Å)	i	8.691 (6)	8.735 (2)	8.775 (4)	8.780 (6)
	f	8.779 (7)	8.801 (4)	8.814 (6)	8.815 (5)
b (Å)	i	13.253 (6)	13.307 (2)	13.349 (4)	13.368 (5)
	f	13.438 (7)	13.563 (4)	13.701 (6)	13.720 (5)
c (Å)	i	9.532 (5)	9.565 (2)	9.545 (3)	9.555 (4)
	f	9.474 (5)	9.466 (3)	9.425 (5)	9.425 (4)
β ( )	i	96.32 (8)	96.48 (3)	96.84 (5)	96.79 (8)
	f	98.52 (9)	98.02 (6)	98.79 (8)	98.79 (7)
V (Å^3)	i	1092 (1)	1104.7 (4)	1110.1 (7)	1114 (1)
	f	1105 (1)	1118.9 (7)	1125 (1)	1126.5 (9)
V_{cav} (Å^3)		11.56	11.71	12.78	13.94
k_{fit} (10^{-6} s^{-1})		5.6	11	15	37
Without Xe lamp		1.0	1.7	2.4	2.4

Packing potential energy

The packing potential energy (PPE) was calculated for each crystal structure using the *OPEC* package (Gavezzotti, 1983). Pairwise potentials were applied, which are functions of interatomic distances. The C—H distance was set to 1.08 Å. Atom pairs within 7 Å separation were included but the pairs associated by a hydrogen bond were omitted because electro-

Fig. 5. Change of the unit-cell dimensions of the S-S-pea(I) complex at 296 K. Solid curves represent the first-order kinetics and dotted lines indicate the final parameters.
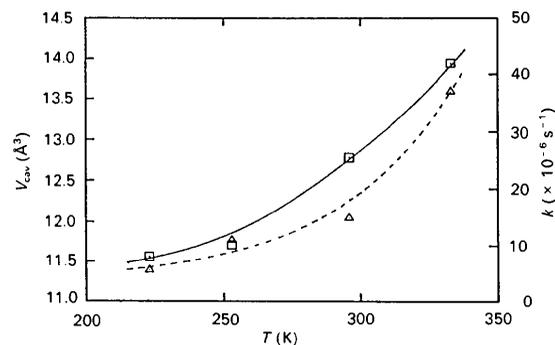
Fig. 6. Temperature dependence of the reaction rate (triangles, dashed line; k in $\times 10^{-6}$ s^{-1}) and the volume of the reaction cavity (squares, solid line; V_{cav} in Å^3).
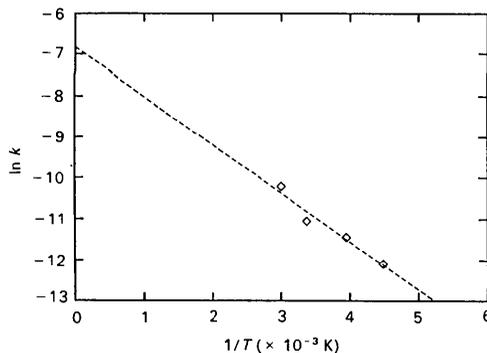
Fig. 7. Arrhenius plot for the S-S-pea(I) complex.

static potential was not considered. The Co atom was regarded as a C atom because of the lack of reliable parameters for the Co atom. The results are listed in Table 7.

The potential energy for the S-S-pea(I) complex at the final stage at 296 K was -190 kJ mol^{-1}, which is about 9 kJ mol^{-1} higher than that of the initial structure at the same temperature. The cause of this difference in packing potential energy is mainly not the repulsion by the inverted ce group but the loss of the attraction by the vacancy induced by the reaction. The packing potential energy represents the enthalpy term in the total energy. The entropy term associated with the racemization of the ce group is about 1.7 kJ mol^{-1} at room temperature and cannot override the gap in the enthalpy term at the ground state though the replacement was carried out for the Co atom. However, the entropy term may be a driving force at the excited state.

The packing potential energy was calculated for the final structure of S-S-pea(I) using the original cell dimensions. The value was -160 kJ mol^{-1}, which is 30 kJ mol^{-1} higher than that in the final cell. This energy was released by the cell change.

The packing potential energy was also calculated for the imaginary racemic structure of an $(S + R)$-S-pea(II) crystal at 296 K. This structure was generated by inverting half of the methyl group in the ce group around the cyano group. The packing potential energy for this structure was calculated to be $+543$ kJ mol^{-1}. This value is about 755 kJ mol^{-1} higher than the chiral S-S-pea(II) structure at 296 K. The racemization seems to be impossible for the S-S-pea(II) crystal.

Table 7. *Packing potential energy* $(PPE$; kJ mol^{-1}) *of S-S-pea*(I) *and S-S-pea*(II) *complexes*

T (K)		S-Spea(I) Initial		Final		S-S-pea(II)	
T (K)	223	253	296	333	296	223	296
PPE (kJ mol^{-1})	-201	-199	-199	-196	-190	-212	-212

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Crystal Chemistry and Physical Properties of a Series of N-Substituted (Thio)Morpholinium Di-7,7,8,8-tetracyano-p-quinodimethanides

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Abstract

Crystal structures of a series of the title compounds are compared. Classes I, II and II' with 2, 4 and 8 tetracyanoquinodimethane (TCNQ) moieties per translation period, respectively, are distinguished.

For class I a subclassification is made according to: the number of inequivalent stacks (1 or 2); cation disorder [dynamic (d) or static (s)]; and chain directions [parallel (p) or crossed (c)]. Crystals of classes II and II' appear to be of type $(1,d,p)$. Disorder of the cations is a frequent phenomenon. Generally,