and it can be clearly seen that the value of Σ is indeed 15 and in agreement with our calculations. Approximately 20% of the results obtained by use of Gertsman's algorithm contain an error of a factor of either 2 or $\frac{1}{2}$ in the value of Σ. This appears to be related to the determination of ξ, the components of which are given without derivation in his paper. We are therefore unable to identify the exact nature of the error.

Concluding remarks

We have generated tables of coincidence orientations, CSL, DSC and step vectors for the ordered tetragonal $L1_0$ alloys for the primitive tetragonal cell based on the pseudo-b.c.t. description with $\Sigma \leq 50$ and $0.800 \leq 2^{1/2}c/a \leq 1.900$. We have made use of the conditions given in (7) and (16) to ensure the completeness of our results. We have also shown that the rules for the determination of Σ for tetragonal crystals given in Gertsman (1990) do not always give the correct value. The data to be deposited comprise a comprehensive list of Σ values, axes, angles, CSLs, DSCs and step vectors for $L1_0$ alloys for $\Sigma \leq 50$ and $0.800 \leq 2^{1/2}c/a \leq 1.900$.*

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* Lists of Σ values, axes, angles, CSLs, DSCs and step vectors for $L1_0$ alloys for $\Sigma \leq 50$ with $0.800 \leq 2^{1/2}c/a \leq 1.900$ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55719 (258 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bruggeman, G. A., Bishop, G. H. & Hartt, W. H. (1972). *The Nature and Behavior of Grain Boundaries*, edited by H. Hu, p. 83. New York: Plenum.
Chen, F. R. & King, A. H. (1987). *Acta Cryst.* **B43**, 416–422.
Chen, F. R. & King, A. H. (1988). *Philos. Mag.* **A57**, 431–455.
Clark, W. A. T., Wagoner, R. H., Chen, Z. Y., Lee, T. C., Robertson, I. M. & Birnbaum, H. K. (1992). *Scr. Metall.* **26**, 203–206.
Du Val, P. (1964). *Homographies, Quaternions and Rotations*, Oxford Mathematical Monographs. Oxford: Clarendon Press.
Fukutomi, H., Kamijo, T. & Horiuchi, R. (1986). *Trans. Jpn Inst. Met. Suppl.* pp. 929–936.
Gertsman, V. Yu. (1990). *Colloq. Phys.* **C-1**, 145–150.
Grimmer, H. (1974). *Acta Cryst.* **A30**, 685–688.
Grimmer, H. (1980). *Acta Cryst.* **A36**, 382–389.
Grimmer, H. (1989). *Acta Cryst.* **A45**, 320–325.
Grimmer, H. (1992*a*). Private communication.
Grimmer, H. (1992*b*). *Mater. Forum*. In the press.
Grimmer, H. & Warrington, D. H. (1987). *Acta Cryst.* **A43**, 232–243.
King, A. H. (1982). *Acta Metall.* **30**, 419–427.
Shin, K. & King, A. H. (1991). *Philos. Mag.* **A63**, 1023–1033.
Singh, A., Chandrasekhar, N. & King, A. H. (1990). *Acta Cryst.* **B46**, 117–125.
Watanabe, T. (1984). *Res. Mech.* **11**, 47–84.

Acta Cryst. (1993). B49, 272–277

Crystalline-State Racemization of a Chiral Cyanoethyl Group Connected by a Hydrogen Bond

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Abstract

The crystal of [(*R*)-1-cyanoethyl]bis(dimethylglyoximato)(pyrrolidine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato) revealed a gradual change of cell parameters keeping the single-crystal form when it was irradiated by X-rays. It contains one water molecule as solvent in the asymmetric unit. The reactive cyanoethyl group is hydrogen bonded to the water molecule. In spite of the

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restriction by the hydrogen bond, the ordered chiral cyanoethyl group is converted to disordered racemates without degradation of crystallinity. The rate of the racemization can be explained well by the cavity size of the cyanoethyl group.

Introduction

It has been found that the chiral 1-cyanoethyl (ce) group bonded to a cobalt atom in crystals of bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes with various bases as axial ligands is racemized by X-ray exposure without degradation of the crystallinity (Ohashi, 1988, and references therein). This type of solid-state reaction is termed a crystalline-state racemization. A good correlation between the reaction rate and the volume of the reaction cavity, the void space around the reactive group, has been obtained for the above cobaloxime complex crystals.

Among the above crystals the ce group of [(*R*)-1-cyanoethyl](triphenylphosphine)cobaloxime (*R*-tpp) was not racemized by X-ray exposure at room temperature. It was assumed that two factors may be responsible for the non-reactivity of the crystal; one is the insufficient size of the reaction cavity, the other is hydrogen-bond formation between the ce group and the solvent water molecule. Although other crystals with such a hydrogen bond had not been obtained previously, it was expected that the non-reactivity would be caused by the small cavity (Kurihara, Uchida, Ohashi, Sasada, Ohgo & Baba, 1983). However, it was found that the hydrogen bond between the reactive group and the solvent molecule has an important role in increasing the rate of solid-state photoisomerization relative to those for crystals which lack such hydrogen bonds (Sekine & Ohashi, 1991).

Recently a crystal of [(*R*)-1-cyanoethyl](pyrrolidine)cobaloxime (*R*-pyrr) has been prepared. The preliminary investigation revealed that it contained one water molecule as solvent in the asymmetric unit, but that its cell dimensions were gradually changed by X-ray exposure. This work was undertaken to elucidate the role of the hydrogen bond in the crystalline-state racemization.

Experimental

Dark-red crystals of *R*-pyrr were grown from an aqueous methanol solution by the method reported previously (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981).

Changes of cell dimensions with exposure time were measured on a Rigaku AFC-4 four-circle diffractometer with Mo $K\alpha$ radiation monochromated by graphite (40 kV, 20 mA, $\lambda = 0.7107$ Å). The determination of cell dimensions was repeated continuously using 15 2θ values in the range $20 \leq 2\theta \leq 30°$. The exposure time was monitored by a clock which ran when the X-ray window shutter was open. These conditions are the same as those for other cobaloxime crystals reported previously. Crystal data: $[Co(C_3H_4N)(C_4H_7N_2O_2)_2(C_4H_9N)].H_2O$, $M_r = 432.4$, orthorhombic, $P2_12_12_1$, $Z = 4$, $D_m = 1.42$, $D_x = 1.42$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.832 mm^{-1}, $F(000) = 912$, $T = 296$ K, $a = 12.883\,(2)$, $b = 13.355\,(2)$, $c = 11.706\,(3)$ Å, $V = 2014.1\,(7)$ Å^3, at the initial stage, and $a = 13.177\,(2)$, $b = 13.120\,(2)$, $c = 11.694\,(2)$ Å, $V = 2021.6\,(5)$ Å^3 at the final stage.

Three-dimensional data collection was carried out at the initial and final stages of the reaction. At the initial stage, a crystal 0.4 × 0.2 × 0.1 mm was used. Intensity data were collected up to $\sin\theta/\lambda \leq 0.65$ Å^{-1} ($0 \leq h \leq 16$, $0 \leq k \leq 17$, $0 \leq l \leq 15$) by means of an ω–2θ scan technique at 8° min^{-1} in 2θ. A total of 2618 reflexions were measured, of which 2545 with $|F| > 3\sigma(F)$ were used for the structure determination. About 20 h were required for the data collection. The structure factors of three monitor reflexions varied by no more than 3.7% during data collection and a correction for crystal decay was not applied. Unit-cell parameters were determined before and after data collection. They were changed to $a = 12.944\,(3)$, $b = 13.300\,(3)$, $c = 11.728\,(4)$ Å, $V = 2019\,(1)$ Å^3 after the collection. The average values, $a = 12.909\,(3)$, $b = 13.327\,(3)$, $c = 11.717\,(4)$ Å, $V = 2016\,(1)$ Å^3, were used for the structure analysis.

In order to obtain the racemic crystal, the crystal was continuously exposed to Mo $K\alpha$ radiation (50 kV, 150 mA) until changes in the cell dimensions became smaller than their standard deviations. This required about 800 h. This crystal (spherical with a diameter of 0.4 mm) was used for the data collection at the final stage. Half of the reciprocal space was examined up to $\sin\theta/\lambda \leq 0.65$ Å^{-1} ($-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $0 \leq l \leq 15$). The structure factors of three monitor reflexions did not vary by more than 2%. Equivalent reflexions were averaged, $R_{\rm int} = 0.046$. A total of 4827 reflexions were measured, of which 4622 with $|F| > 3\sigma(F)$ were used. The other conditions were the same as those of the initial stage. The space group did not change in the process of the reaction.

The initial structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least squares (*SHELX*76; Sheldrick, 1976) based on F with $w = [\sigma^2(|F_o|) + 0.029|F_o|^2]^{-1}$. Anisotropic thermal parameters were applied to non-H atoms. H atoms belonging to the methyl group were located by the geometric calculation, other H atoms were refined isotropically with constraints on C—H=N—H = 1.00 Å and O—H =

0.96 Å. A total of 315 parameters were refined. Final R and wR were 0.037 and 0.055, respectively, $S = 0.90$, $(\Delta/\sigma)_{\max} = 0.96$. No peak higher than 0.45 e Å^{-3} was found in the difference map. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final structure was obtained by full-matrix least-squares refinement with $w = [\sigma^2(|F_o|) + 0.014|F_o|^2]^{-1}$ using the values of the initial structure. Peaks corresponding to the S-ce group were found on the difference map and the parameters of the ce group were treated as a disordered structure. The site occupancy of each ce group was fixed to 0.5. The non-H atoms were refined anisotropically except that the C(13), C(15) and N(6) atoms of the ce groups were refined isotropically. H atoms were treated by the same method as the initial structure but the H atoms bonded to C(13) were not included. A total of 302 parameters were refined. Final R and wR values were 0.053 and 0.082, respectively, $S = 0.61$, $(\Delta/\sigma)_{\max} = 0.90$. No peak higher than 0.64 e Å^{-3} was found in the difference map. No absorption and extinction corrections were applied. The atomic parameters for non-H atoms of the initial and final structures are given in Table 1.*

Discussion

Molecular and crystal structure

The molecular structure at the initial stage and the numbering of the atoms is shown in Fig. 1. Selected bond distances, bond angles and torsion angles at the initial stage are listed in Table 2. Bond distances and angles are approximately the same as those in the cobaloxime complexes determined so far. The ce group revealed a disordered structure at the final stage, as shown in Fig. 2. Such an order–disorder transformation is classified in the first mode, that is, there is one molecule in the asymmetric unit and the ce group is changed to the disordered racemates (Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1985). The N atom of the ce group is connected to the solvent water molecule by a hydrogen bond, which is conserved in the racemization. A similar hydrogen bond was observed in the crystal of R-tpp, which is also shown in Fig. 2. Except for the disordered ce group, the corresponding bond distances and angles did not vary during the racemization.

Table 1. *Atomic coordinates* ($\times 10^5$ *for* Co, $\times 10^4$ *for other atoms*) *and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms*

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(*a*) Initial structure				
Co	51945 (3)	97865 (3)	94964 (3)	2.2
N(1)	4483 (2)	9486 (2)	8134 (2)	2.8
N(2)	5998 (2)	10546 (2)	8486 (3)	2.7
N(3)	5903 (2)	10099 (2)	10872 (2)	2.7
N(4)	4380 (2)	9027 (2)	10518 (2)	2.8
O(1)	3663 (2)	8879 (2)	8106 (2)	3.7
O(2)	6846 (2)	11073 (2)	8823 (3)	3.8
O(3)	6730 (2)	10717 (2)	10901 (2)	3.7
O(4)	3560 (2)	8442 (2)	10211 (3)	4.3
C(1)	4788 (3)	9961 (3)	7219 (3)	3.3
C(2)	5708 (3)	10570 (3)	7430 (3)	3.2
C(3)	5502 (3)	9750 (3)	11801 (3)	3.1
C(4)	4619 (3)	9097 (3)	11594 (3)	3.2
C(5)	4265 (4)	9860 (4)	6089 (3)	4.9
C(6)	6279 (4)	11168 (4)	6540 (4)	4.8
C(7)	5908 (4)	10042 (4)	12956 (3)	4.5
C(8)	4062 (4)	8533 (5)	12502 (4)	5.6
N(5)	4241 (2)	10982 (2)	9868 (2)	2.6
C(9)	4668 (3)	12021 (3)	9816 (4)	4.1
C(10)	3733 (3)	12704 (3)	10073 (4)	4.4
C(11)	2790 (3)	12097 (3)	9677 (4)	4.2
C(12)	3230 (3)	11089 (3)	9293 (4)	3.7
C(13)	6238 (3)	8638 (3)	9266 (3)	3.8
C(14)	6293 (4)	8144 (4)	8123 (4)	5.6
C(15)	6123 (4)	7883 (3)	10145 (4)	4.7
N(6)	6027 (4)	7278 (3)	10833 (4)	7.1
O*W*	6607 (3)	5965 (3)	12695 (3)	5.8
(*b*) Final structure				
Co	51179 (3)	97808 (3)	94265 (4)	2.7
N(1)	4401 (3)	9504 (2)	8063 (3)	3.3
N(2)	5943 (3)	10520 (3)	8408 (3)	3.4
N(3)	5847 (2)	10066 (3)	10786 (3)	3.4
N(4)	4296 (3)	9063 (3)	10451 (3)	3.4
O(1)	3577 (3)	8908 (3)	8046 (3)	4.5
O(2)	6773 (2)	11032 (3)	8746 (3)	4.5
O(3)	6674 (2)	10652 (3)	10801 (3)	4.8
O(4)	3466 (3)	8488 (3)	10167 (3)	5.0
C(1)	4724 (3)	9948 (3)	7137 (3)	3.7
C(2)	5651 (4)	10543 (3)	7353 (4)	3.8
C(3)	5456 (3)	9722 (4)	11728 (4)	4.0
C(4)	4546 (4)	9114 (4)	11535 (4)	4.0
C(5)	4208 (5)	9841 (5)	6020 (4)	5.5
C(6)	6224 (5)	11116 (5)	6451 (5)	5.6
C(7)	5873 (5)	9998 (6)	12884 (4)	6.1
C(8)	3981 (5)	8534 (6)	12443 (5)	6.6
N(5)	4237 (2)	11038 (2)	9792 (3)	3.3
C(9)	4679 (4)	12077 (3)	9730 (6)	5.1
C(10)	3777 (5)	12807 (4)	9937 (9)	7.8
C(11)	2833 (4)	12167 (4)	9609 (6)	5.7
C(12)	3234 (4)	11146 (4)	9229 (5)	4.8
C(13)	6186 (7)	8639 (6)	9265 (7)	4.6 (2)
C(13′)*	5868 (5)	8430 (4)	9059 (5)	2.8 (1)
C(14)	6250 (11)	8117 (8)	8120 (6)	7.0
C(14′)	6966 (5)	8568 (6)	8633 (8)	4.5
C(15)	6072 (8)	7893 (6)	10193 (7)	3.9 (2)
C(15′)	5840 (7)	7727 (6)	10020 (8)	4.1 (2)
N(6)	6097 (9)	7385 (7)	10951 (7)	5.9 (2)
N(6′)	5819 (7)	7183 (5)	10755 (7)	4.6 (2)
O*W*	6563 (3)	6055 (5)	12778 (4)	8.0

* The occupancy factors of the primed pairs of atoms are all 0.5.

The crystal structure viewed along the a axis at the initial stage is shown in Fig. 3. The cobaloxime complexes and water molecules make a three-dimensional network with the hydrogen bonds: N(6)···OW [2.895 (6) Å] and OW···O(1) [2.823 (5) Å], which connect the molecules related by 2_1 symmetry along the a axis, N(6)···OW and OW···N(5) [3.058 (4) Å], along the b axis, and O(1)···OW and OW···N(5), along the c axis.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond distances and angles, and hydrogen-bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55671 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0610]

Table 2. *Selected bond distances* (Å), *angles* (°) *and torsion angles* (°) *in the initial structure*

Co—N(1)	1.886 (3)	Co—N(4)	1.889 (3)
Co—N(2)	1.872 (3)	Co—N(5)	2.059 (3)
Co—N(3)	1.901 (3)	Co—C(13)	2.057 (4)
N(1)—Co—N(2)	81.3 (1)	N(2)—Co—C(13)	87.4 (1)
N(1)—Co—N(3)	179.5 (1)	N(3)—Co—N(4)	81.3 (1)
N(1)—Co—N(4)	98.7 (1)	N(3)—Co—N(5)	86.5 (1)
N(1)—Co—N(5)	92.9 (1)	N(3)—Co—C(13)	87.6 (1)
N(1)—Co—C(13)	93.0 (1)	N(4)—Co—N(5)	86.9 (1)
N(2)—Co—N(3)	98.7 (1)	N(4)—Co—C(13)	92.9 (1)
N(2)—Co—N(4)	179.7 (1)	N(5)—Co—C(13)	174.1 (1)
N(2)—Co—N(5)	92.8 (1)	C(14)—C(13)—C(15)	109.7 (4)
N(2)—Co—N(5)—C(9)	−29.9 (3)	N(1)—Co—C(13)—C(14)	13.6 (3)
N(1)—Co—N(5)—C(12)	16.9 (3)	N(4)—Co—C(13)—C(15)	−15.6 (3)

Racemization rate and reaction cavity

Fig. 4 shows the variation in the cell dimensions with exposure time. It indicates that the variation follows first-order kinetics. The rate constants are calculated by least-squares fitting for the *a* and *b* axes, since changes in the other dimensions are not so significant. The calculated values are 1.77×10^{-6} and $1.61 \times 10^{-6}\,s^{-1}$ for *a* and *b*, respectively. The average value is $1.69 \times 10^{-6}\,s^{-1}$.

It has been proposed that the packing around the ce group plays an important role in determining the reactivity and that this can be estimated from the size of the reaction cavity, which is defined as the space limited by a concave surface of the spheres of the surrounding atoms around the reactive group in the crystal. The radius of each sphere is taken to be 1.2 Å greater than the van der Waals radius of the corresponding atom (Ohashi, Uchida, Sasada & Ohgo, 1983). The cavity for the ce group of the present complex is shown in Fig. 5. The N atom is out of the cavity since it makes a hydrogen bond with the water molecule. A similar cavity was obtained for *R*-tpp, which is also given in Fig. 5.

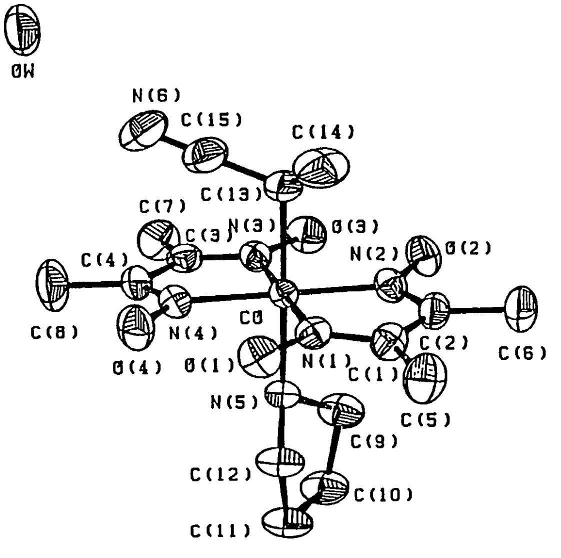

Fig. 1. Molecular structure at the initial stage with the numbering of atoms.

The size of the cavity was calculated to be 11.6 $Å^3$ for *R*-pyrr, which is greater than that for *R*-tpp (11.3 $Å^3$) by 0.3 $Å^3$. The difference in cavity size explains the difference in the reactivity of the crystals at room temperature well. The crystals of [(*R*)-1-cyanoethyl][(*S*)-1-phenylethylamine]cobaloxime (*R*-*S*-pea; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), [(*S*)-1-cyanoethyl][(*S*)-1-phenylethylamine]cobaloxime (*S*-*S*-pea; Ohashi, Sasada & Ohgo, 1978), [(*R*)-1-cyanoethyl](tributylphosphine)cobaloxime (*R*-tbp; Kurihara, Uchida, Ohashi, Sasada, Ohgo & Baba, 1983), [(*R*)-1-cyanoethyl](diphenylethylphosphine)cobaloxime (*R*-dpep; Tomotake,

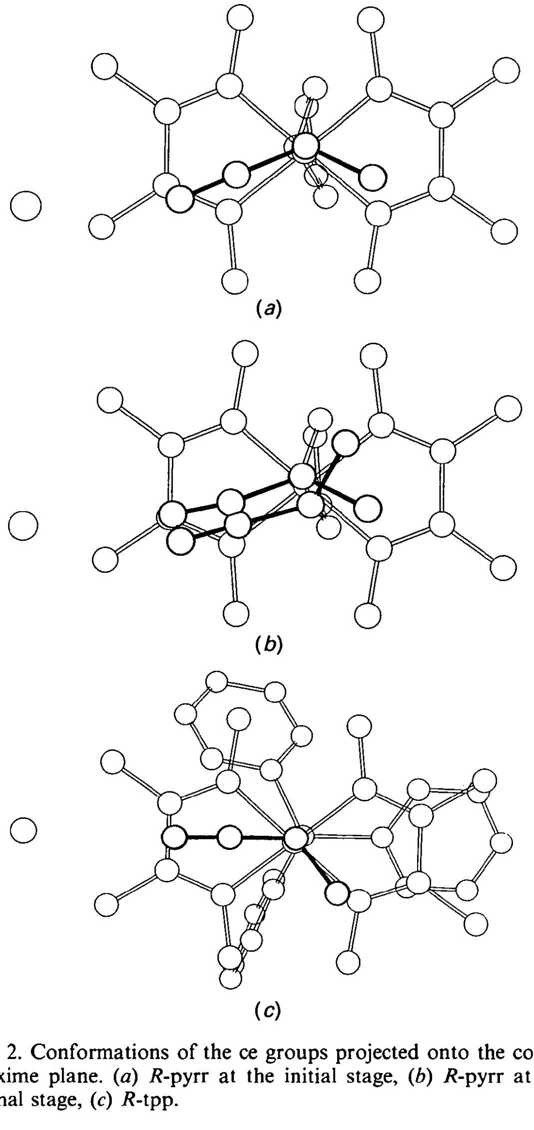

Fig. 2. Conformations of the ce groups projected onto the cobaloxime plane. (*a*) *R*-pyrr at the initial stage, (*b*) *R*-pyrr at the final stage, (*c*) *R*-tpp.

Uchida, Ohashi, Sasada, Ohgo & Baba, 1984), [(*R*)-1-cyanoethyl](diethylphenylphosphine)cobaloxime (*R*-depp; Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1984), [(*R*)-1-cyanoethyl](dimethylphenylphosphine)cobaloxime (*R*-dmpp; Kojima, Iwasaki, Ohashi, Baba & Ohgo, 1991) also have one molecule in the asymmetric unit and their crystalline-state racemizations may belong to the first mode if they occur. Table 3 lists the reactivity of the crystals belonging to the first mode. The four crystals, *R*-tpp, *R*-tbp, *R*-dpep and *R*-depp are non-reactive at room

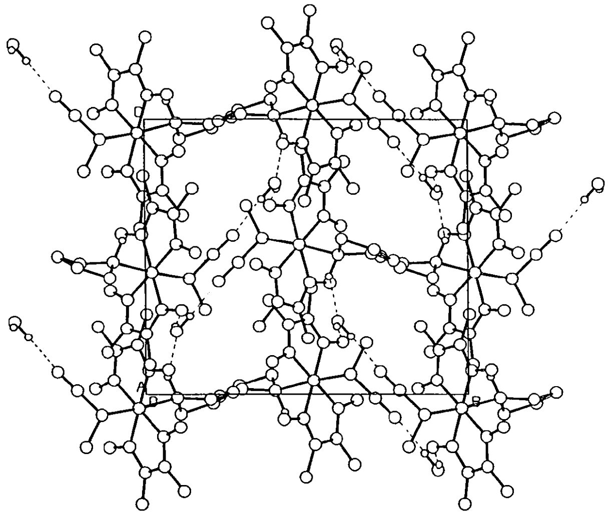

Fig. 3. Crystal structure at the initial stage viewed along the *a* axis. Dotted lines indicate hydrogen bonds.

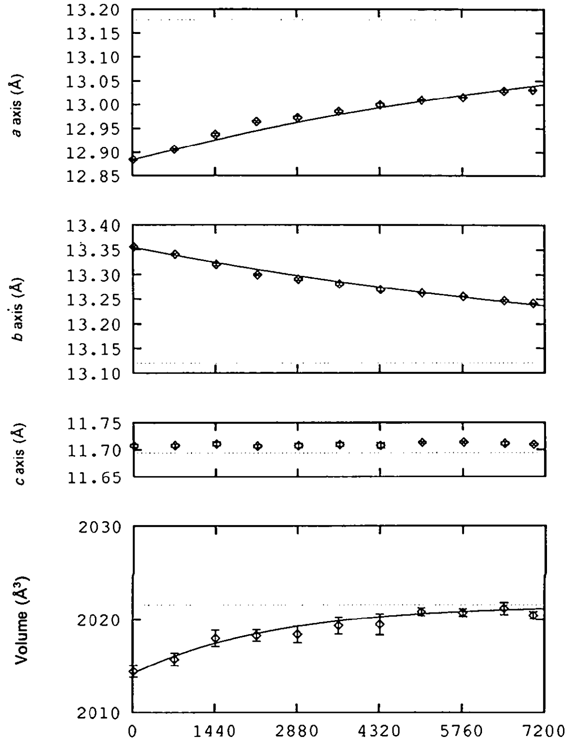

Fig. 4. Change of the unit-cell dimensions on exposure to X-rays. Solid curves represent the first-order kinetics and dotted lines indicate the final parameters. The rate constant of the *c* axis could not be determined.

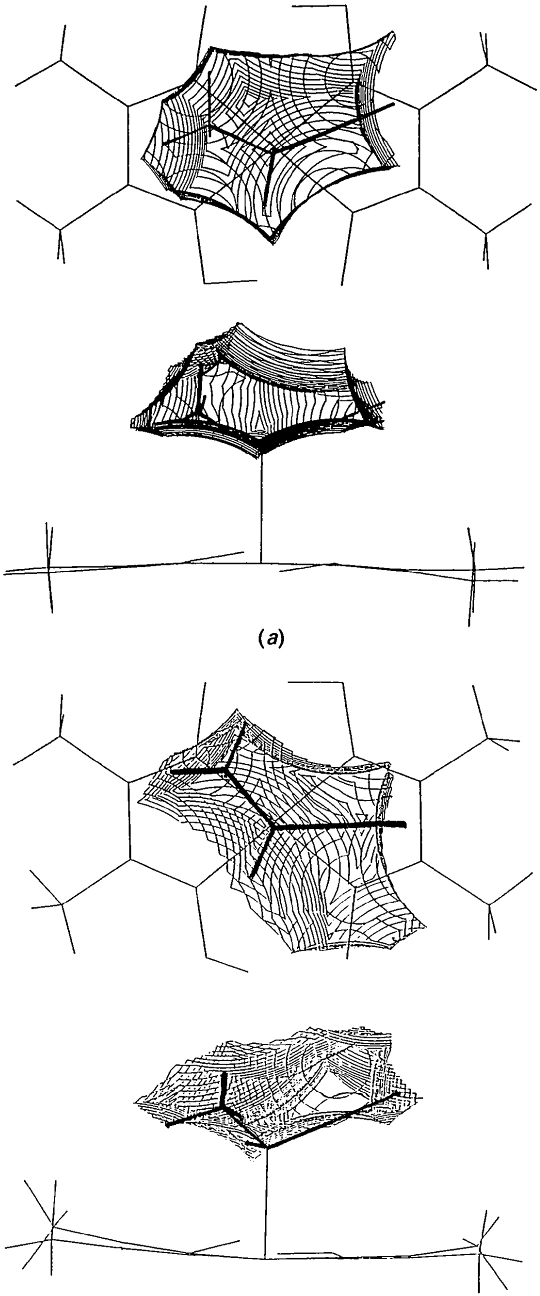

Fig. 5. Reaction cavities projected onto the cobaloxime planes and their side views. Contours are drawn in sections separated by 0.1 Å. (*a*) At the initial stage of *R*-pyrr, (*b*) *R*-tpp.

Table 3. *The size of the reaction cavity and reaction rate for some cobaloxime complexes*

	V (Å^3)	Reaction rate ($\times 10^{-6}$ s^{-1})
R-depp	8.40	–*
R-dpep	10.18	–
R-tbp	10.64	–
R-tpp	11.31	–
R-pyrr	11.55	1.69
S-*S*-pea	12.23	2.38
R-*S*-pea	14.53	3.13
R-dmpp	17.97	4.80†

* Racemization was not observed at room temperature.

† Value determined from the site occupancy of ce group.

temperature. This table clearly indicates that the larger the reaction cavity is, the greater the reaction rate. A volume greater than 11.5 Å^3 appears necessary for racemization.

The above results suggest that the reactivity of the ce group depends on the size of the cavity and that the hydrogen bond may play no role in the racemization. In the β–α solid-state photoisomerization, the β-ce group bonded to the cobalt atom was changed to an α-ce group. If the N atom of the β-ce group was connected by a hydrogen bond with the solvent molecule, the isomerization rate became faster. It was proposed that the hydrogen bond would stabilize the β-ce radical produced by the Co—C bond cleavage and that it may accelerate the β–α radical transformation (Sekine & Ohashi, 1991). In the racemization, on the other hand, the α-ce radical, produced by the Co—C bond breaking, may be stable and may not be affected by the hydrogen bond. Therefore, the reaction rate depends only on the size of the cavity for the ce group.

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References

Kojima, Y., Iwasaki, S., Ohashi, Y., Baba, S. & Ohgo, Y. (1991). *Acta Cryst.* **C47**, 300–303.

Kurihara, T., Uchida, A., Ohashi, Y., Sasada, Y., Ohgo, Y. & Baba, S. (1983). *Acta Cryst.* **B39**, 431–437.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Ohashi, Y. (1988). *Acc. Chem. Res.* **21**, 268–274.

Ohashi, Y., Sasada, Y. & Ohgo, Y. (1978). *Chem. Lett.* pp. 743–746.

Ohashi, Y., Uchida, A., Sasada, Y. & Ohgo, Y. (1983). *Acta Cryst.* **B39**, 54–61.

Ohashi, Y., Yanagi, K., Kurihara, T., Sasada, Y. & Ohgo, Y. (1981). *J. Am. Chem. Soc.* **103**, 5805–5812.

Ohgo, Y., Takeuchi, S., Natori, Y., Yoshimura, J., Ohashi, Y. & Sasada, Y. (1981). *Bull. Chem. Soc. Jpn*, **54**, 3095–3099.

Sekine, A. & Ohashi, Y. (1991). *Bull. Chem. Soc. Jpn*, **64**, 2183–2187.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Tomotake, Y., Uchida, A., Ohashi, Y., Sasada, Y., Ohgo, Y. & Baba, S. (1984). *Acta Cryst.* **C40**, 1684–1687.

Tomotake, Y., Uchida, A., Ohashi, Y., Sasada, Y., Ohgo, Y. & Baba, S. (1985). *Isr. J. Chem.* **25**, 327–333.

Acta Cryst. (1993). **B49**, 277–282

Structure of Bis(2-amino-5-nitropyridinium) Dichromate as a Step Towards the Design of Efficient Organic–Inorganic Non-Linear Optical Crystals

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Abstract

The orthorhombic crystal structure of $2C_5H_6N_3O_2^+ \cdot Cr_2O_7^{2-}$ [$a = 22.454$ (6), $b = 15.129$ (2), $c = 5.189$ (2) Å, $Z = 4$, orthorhombic, $P2_1nb$, $D_x = 1.866$ g cm^{-3}] has been solved using direct methods and refined to $wR = 0.029$ for 2514 reflections. This study provides a step towards a new route to obtain non-linear optical crystals which aims at combining the highly polarizable 2-amino-5-nitropyridinium cation with inorganic anionic host matrices. The shielding effect of dichromate anions in the building of an acentric polar framework is discussed. The structure is compared with other structures containing 2-amino-5-nitropyridine moieties. The cations are completely or partly arranged in a 'herringbone' structure in all these frameworks.

Introduction

Research into very effcient and highly transparent non-linear optical crystals (range: 100 nm to IR

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