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Solid State Photoisomerization of But-3-en-1-yl Group in Cobalt Complexes

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The but-3-en-1-yl group bonded to the cobalt atom in some cobaloxime complexes is isomerized to the but-2-en-1-yl group in the solid state on exposure to a xenon lamp. In order to make clear the relationship between the reaction rate and the crystal structure, six complexes with different axial base ligands were prepared; piperidine, **1**, 1-vinylimidazole, **2**, pyrrolidine, **3**, 1-methylimidazole, **4**, 4-*t*-butylpyridine, **5**, and triphenylphosphine, **6**. The crystal structures were determined by X-ray analyses and the reaction rates were estimated from the change of the ^{1}H NMR spectra observed in several intermediate stages. One of the photo products, which has 1-vinylimidazole as an axial base ligand, **7**, was prepared separately and its crystal structure was also analyzed. A pair of the but-3-en-1-yl groups are in contact with each other around an inversion center in the crystal structures of **2**, **5**, and **6**, whereas the but- 3-en-1-yl groups in **1**, **3**, and **4** are isolated from the other but-3-en-1-yl groups of the neighboring molecules in their crystal structures. The reaction rates of the former complexes are significantly greater than those of the latter complexes, except **2**. This suggests that the cooperative motion of the but-3-en-1-yl groups plays an important role in the process of the isomerization. A pair of the but-3-en-1-yl groups around an inversion center in **2** are too closely packed for the isomerization to occur even if the cooperative motion is taken into account.

The (alkyl)bis(dimethylglyoximato)cobalt(III), cobaloxime, complex is one of the model compounds of vitamin B_{12} coenzyme (adenosylcobalamin), a naturally occurring organometallic compound. It has been thought that the fission of the Co–C bond is a trigger for the vitamin B_{12} dependent-enzymatic reactions. Extensive studies have been carried out to examine the mechanisms of light- or thermal-induced cleavage of the Co–C bond in cobaloxime complexes.[1)]

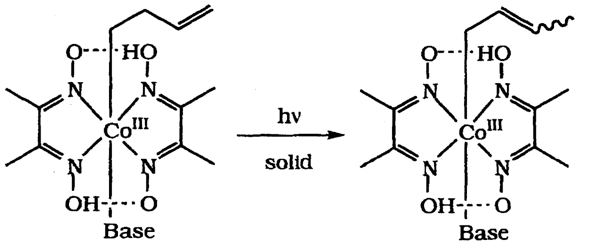
The photo reactivity of the alkyl group bonded to the cobalt atom in the cobaloxime in solid and crystalline state has been extensively studied; for example, racemization of chiral groups such as 1-cyanoethyl,[2)] 1-methoxycarbonylethyl,[3)] 1,2-bis(methoxycarbonyl)ethyl,[4)] 1,2-bis(ethoxycarbonyl)ethyl,[5)] 1,2-bis(allyloxycarbonyl)ethyl groups,[6)] 2-1 isomerization such as 2-cyanoethyl[7)] and 2-methoxycarbonylethyl groups,[8)] and 3-1 isomerization of 3-cyanopropyl group.[9)] The 2-1 and 3-1 isomerizations have been attracting our attention because a chiral alkyl group is produced from an achiral one.[10)] The mechanism of the racemization has been clarified by neutron diffraction using the complex crystal, in which the deuterium atom was replaced with a hydrogen atom bonded to the chiral carbon of the 1-cyanoethyl group.[11)]

In the previous paper,[12)] it was reported that the *trans–cis* isomerization of the but-2-en-1-yl group in some cobaloxime complexes proceeds with retention of the single crystal form on exposure to visible light. Although the conversion was very clear, the mechanism was somewhat obscure. To analyze the isomerization process more precisely, a series of cobaloxime complexes with the but-3-en-1-yl group as an alkyl group were prepared and their photoreactions in the crystalline state were examined, since the group may change to the but-2-en-1-yl group. Moreover the but-3-en-1-yl group is the same as the 2-cyanoethyl group if the C=C double bond is replaced with the cyano group. Recently it was reported that the reversible carbon skeleton rearrangement of the but-3-en-1-yl group occurs in a $CDCl_3$ solution.[13)] The authors claimed that the rearrangement proceeded via a homoallylic intermediate and a cyclopropylmethyl group.

This paper reports a novel solid state isomerization of the but-3-en-1-yl group to the but-2-en-1-yl group and discusses the relationship between the crystal structures and the reaction rates in six cobaloxime complexes which have piperidine, **1**, 1-vinylimidazole, **2**, pyrrolidine, **3**, 1-methylimidazole, **4**, 4-*t*-butylpyridine, **5**, and triphenylphosphine, **6**, as axial base ligands (Scheme 1). The crystal structure of the product **7**with the but-2-en-1-yl group was analyzed to compare with that of **2**.

Experimental

Preparation of 1—6: Each cobaloxime complex with the but-3-en-1-yl group and pyridine as axial ligands was prepared in a similar way.[14)] The complexes **1—6** were prepared from the pyridine complex by changing the axial base ligand. For example, **4** was prepared as follows: The amount of 423 mg (1 mmol) of (but-3-en-1-yl)(pyridine)cobaloxime complex was dissolved in 50 ml methanol and the mixture was stirred with 1.2 g of Dowex® 50-80X (50—100 mesh, H form) and 2 ml water overnight. To the filtrate, 0.10 ml of 1-methylimidazole was added and the mixture was evaporated to afford crude product, **4**. ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.48 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 2.14 (s, 12H,



Base
1: piperidine
2: 1-vinylimidazole
3: pyrrolidine
4: 1-methylimidazole
5: 4-*t*-butylpyridine
6: triphenylphosphine

7: 1-vinylimidazole

Scheme 1.

4CH$_3$), 3.63 (s, 3H, CH$_3$), 4.77 (d, J = 10.0 Hz, 1H, vinyl H), 4.90 (d, J = 17.2 Hz, 1H, vinyl H), 5.76 (ddt, J = 10.0, 17.2, 6.4 Hz, 1H, vinyl H), 6.78 (s, 1H imidazole CH), 6.95 (s, 1H, imidazole CH), 7.42 (s, 1H, imidazole CH).

The single crystals of the complexes **1**—**6** suitable for X-ray work were obtained from 1 : 1 methanol–water solution in the dark.

Preparation of 7: *trans*- and *cis*-(But-2-en-1-yl)bis(dimethylglyoximato)(1-vinylimidazole)cobalt(III). To the mixture of 4.76 g of CoCl$_2$·6H$_2$O and 4.68 g of dimethylglyoxime dissolved in 40 ml methanol, 1.60 g of NaOH dissolved in 20 ml of water was added under Ar atmosphere while stirring. 1.81 ml of 1-vinylimidazole, 2.26 ml of 85% *trans*-1-bromobut-2-ene (containing 15% 1-bromobut-3-ene), and 0.76 g NaBH$_4$ dissolved in 20 ml H$_2$O are added successively. Addition of 100 ml water and filtration afforded 5.37 g of a mixture of *trans* and *cis* title compounds (*trans* : *cis* = 3 : 1). In the products, no (but-3-en-1-yl)cobaloxime was detected on ^{1}H NMR. ^{1}H NMR (CDCl$_3$, 270 MHz) δ = 1.15 (d, J = 7.2 Hz, 3H, *cis*-CH$_3$), 1.22 (d, J = 5.2 Hz, 6H, *trans*-CH$_3$), 2.15 (s, 12H, 4CH$_3$), 2.25 (d, J = 7.2 Hz, 1.5H, *trans*-CoCH$_2$), 2.35 (d, J = 10.0 Hz, 0.5H, *cis*-CoCH$_2$), 4.98 (dd, J = 2.0, 9.0 Hz, 1H, vinyl H), 5.28 (dd, J = 2.0, 16.0 Hz, 1H, vinyl H), 5.32 (dd, 1.5H, two *trans*-vinyl H), 5.32 (m, 0.25H, *cis*-vinyl H), 5.61 (m, 0.25H, *cis*-vinyl H), 6.80 (dd, J = 9.0, 16.0 Hz, 1H vinyl H), 7.01 (s, 1H, imidazole H), 7.09 (s, 1H, imidazole H), 7.62 (s, 1H, imidazole H). The complexes with 1-methylimidazole and 4-*t*-butylpyridine were prepared by the same method. However, the complexes with nonaromatic bases (piperidine, pyrrolidine, and triphenylphosphine) were not prepared in this method. The crystals of (but-2-en-1-yl)(1-vinylimidazole)-cobaloxime, **7**, suitable for X-ray work were obtained from an aqueous solution in the dark.

Photoreaction: 50 mg of powdered sample was put into a glass vessel whose radius is 18 mm. The sample was irradiated with a high-flux Xe lamp (San-ei, Super Bright 150) at a distance of 25 mm, through a glass fiber installed on the lamp. Every 2 hours, the sample was stirred, and 5 mg of the sample was taken out from the vessel and dissolved in a chloroform solution. The ^{1}H NMR measurement of the solution showed that the but-3-en-1-yl group has a peak assigned to a vinyl proton at 5.76 ppm. The peak area after t hours exposure was integrated to be $Ir(t)$. The but-2-en-1-yl group has peaks assigned to two vinyl protons at 5.28 ppm, the peak area of which after t hours exposure was integrated to be $Ip(t)$. The conversion rate, $C(t)$, is given by $C(t) = Ir(t)/\{Ir(t)+0.5Ip(t)\}$, from which the values of $C(2)$ to $C(10)$ were estimated. $C(0)$ is, of course, 1.0 since $Ip(0)$ is 0.0.

Crystal Structure Analysis: The crystal data and experimental details are summarized in Table 1. The structures were solved by the direct method with the program SHELXS-86[15] for **1**, **5**, **6**, and **7** with MULTAN[16] for **2**, and by the Patterson method with the program PATTY92[17] for **3** and **4**. The structure refinements were carried out by the full-matrix least-squares with the program SHELXL-93.[18] In the process of the refinement, the but-3-en-1-yl groups were found to be disordered. The bond distances and angles of the disordered but-3-en-1-yl groups were restrained to have ideal values. Non-hydrogen atoms of the disordered but-3-en-1-yl groups were refined isotropically and the others were refined anisotropically. All the hydrogen atoms were generated geometrically by the riding model except those of the hydroxy groups in the cobaloxime moiety. The atomic scattering factors were taken from International Tables for Crystallography.[19] The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Tables 2, 3, 4, 5, 6, 7, and 8 for **1**, **2**, **3**, **4**, **5**, **6**, and **7**. Lists of the anisotropic and isotropic temperature factors U_{ij} and U for non-hydrogen atoms, atomic coordinates and temperature factors for hydrogen atoms, all the bond distances and angles, as well as the observed and calculated structure factors are deposited as Document No. 71059 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results

Photoisomerization. The concentration, $C(t)$, of the (but-3-en-1-yl)cobaloxime at an constant interval of 2 h exposure was estimated from the integration of peaks for the vinyl protons of the but-3-en-1-yl and but-2-en-1-yl groups. Figure 1 shows the plot of $\ln C(t)$ with the exposure time. The figure shows that the reaction rates are well explained by first-order kinetics. The rate constants for **1**, **2**, **3**, **4**, **5**, and **6** were estimated to be 0.5, 0.8, 1.1, 1.4, 3.2, and 3.3×10^{-2} h^{-1}, respectively. The single crystals of **3**, **4**, **5**, and **6** were irradiated with the high- flux Xe lamp through a glass fiber, since the crystals have large reaction rate constants. However, crystal structure analyses by X-rays after the irradiation showed that any structural changes were undetectable.

Crystal Structure. (But-3-en-1-yl)(piperidine)cobaloxime 1: The crystal structure viewed along the a axis and the ORTEP[20] drawing of the molecular structure with

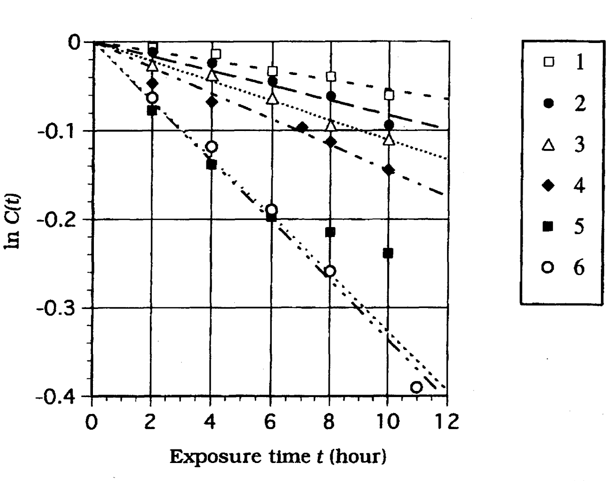


Fig. 1. Reaction rates of (but-3-en-1-yl)cobaloximes. $C(t)$ stands for concentration of the reactant at t hours irradiation. piperidine, **1**, 1-vinylimidazole, **2**, pyrrolidine, **3**, 1-methylimidazole, **4**, 4-*t*-butylpyridine, **5**, and triphenylphosphine, **6**.

Table 1. Crystal Data and Experimental Condition

Axial base	Piperidine (**1**)	1-Vinylimidazole (**2**)	Pyrrolidine (**3**)	1-Methylimidazole (**4**)	4-*t*-Butylpyridine (**5**)	Triphenylphosphine (**6**)	(**7**)
Crystal data							
Chemical formula	$[Co(C_4H_7)(C_4H_7N_2O_2)_2(C_5H_{11}N)]$	$[Co(C_4H_7)(C_4H_7N_2O_2)_2(C_5H_6N_2)]$	$[Co(C_4H_7)(C_4H_7N_2O_2)_2(C_4H_9N)]$	$[Co(C_4H_7)(C_4H_7N_2O_2)_2(C_4H_6N_2)]$	$[Co(C_4H_7)(C_4H_7N_2O_2)_2(C_9H_{13}N)]$	$[Co(C_4H_7)(C_4H_7N_2O_2)_2(C_{18}H_{15}P)]$	$[Co(C_4H_7)(C_4H_7N_2O_2)_2(C_4H_6N_2)]$
Chemical formula weight	429.41	438.38	415.38	426.37	479.46	606.53	438.38
Cell setting	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$	$P2_12_12_1$	Cc	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	9.699(2)	9.708(1)	12.892(2)	13.270(3)	9.354(1)	14.933(3)	10.711(1)
b/Å	16.649(2)	13.3587(1)	16.136(2)	11.674(3)	23.294(4)	13.184(2)	11.689(1)
c/Å	12.842(2)	8.5207(1)	9.664(2)	13.510(3)	11.285(1)	15.320(1)	8.661(1)
α/°	—	101.74(1)	—	—	—	—	108.55(1)
β/°	92.46(1)	102.10(1)	—	103.88(2)	94.34(1)	93.73(1)	100.85(1)
γ/°	—	77.97(1)	—	—	—	—	86.61(1)
V/Å^3	2071(1)	1041(1)	2010(1)	2031(1)	2451(1)	3009(1)	1009.6(2)
Z	4	2	4	4	4	4	2
F(000)	912	460	880	896	1016	1272	460
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	24	25	25	23	25	25
θ range/°	10—12	14—15	14—15	14—15	14—15	14—15	14—15
μ/mm^{-1}	0.86	0.858	0.884	0.878	0.734	0.664	0.878
Temperature/K	296	296	296	295	296	293	295
Crystal form	Plate	Prismatic	Plate	Plate	Prismatic	Cubic	Plate
Crystal size/mm	0.30 × 0.25 × 0.15	0.30 × 0.20 × 0.10	0.5 × 0.3 × 0.2	0.45 × 0.4 × 0.2	0.4 × 0.2 × 0.1	0.3 × 0.2 × 0.2	0.40 × 0.15 × 0.10
Crystal color	Red	Orange	Red	Orange	Orange	Orange	Orange
Data collection							
Diffractometer	Rigaku AFC7	Rigaku AFC7	Rigaku AFC7	Rigaku AFC7	Rigaku AFC7	Rigaku AFC7	Rigaku AFC7
Data collection method	$2\theta/\omega$ scans	$2\theta/\omega$ scans	$2\theta/\omega$ scans	$2\theta/\omega$ scans	$2\theta/\omega$ scans	$2\theta/\omega$ scans	$2\theta/\omega$ scans
Absorption correction	Ψ scans	Ψ scans	Ψ scans	Ψ scans	Ψ scans	Ψ scans	Ψ scans
No. of measured reflections	5213	5073	2621	2437	5972	7172	4881
No. of independent reflections	4933	4794	2621	2437	5641	6915	4632
No. of observed reflections	3720	3236	1843	1683	4210	3640	3202
Criterion for observed reflection	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{max}/°	27.5	27.5	27.5	27.5	27.5	27.5	27.5
Range of h, k, l	$0 \rightarrow 12$ $0 \rightarrow 21$ $-16 \rightarrow 16$	$0 \rightarrow 12$ $-16 \rightarrow 17$ $-11 \rightarrow 10$	$0 \rightarrow 16$ $0 \rightarrow 20$ $0 \rightarrow 12$	$0 \rightarrow 17$ $0 \rightarrow 15$ $-17 \rightarrow 17$	$0 \rightarrow 12$ $0 \rightarrow 30$ $-14 \rightarrow 14$	$0 \rightarrow 19$ $0 \rightarrow 17$ $-19 \rightarrow 19$	$0 \rightarrow 13$ $-15 \rightarrow 15$ $-11 \rightarrow 11$
Refinement							
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2	F^2
$R[F_o > 4\sigma(F_o)]$	0.044	0.043	0.057	0.043	0.041	0.055	0.043
$wR(F^2)$	0.107	0.099	0.154	0.102	0.110	0.120	0.110
S	0.983	1.077	1.102	1.075	0.999	1.134	1.044
Flack's χ parameter	0.00(2)	—	−0.03(6)	−0.03(3)	—	—	—
No. of reflection used in refinement	4933	4794	2616	2437	5615	6915	4632
No. of parameters used	493	259	227	248	284	363	255
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0628P)^2+1.1144P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0464P)^2+4329P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0892P)^2+1.7614P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0559P)^2+0.5784P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0618P)^2+1.8314P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0567P)^2+0.3414P]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0606P)^2+0.5072P]$ where $P=(F_o^2+2F_c^2)/3$
$(\Delta/s)_{max}$	0.001	0.002	0.002	0.008	0.003	0.001	0.002
$\Delta\rho_{max}$/e Å^{-3}	0.417	0.385	0.504	0.332	0.435	0.315	0.339
$\Delta\rho_{min}$/e Å^{-3}	−0.377	−0.295	−0.400	−0.364	−0.462	−0.343	−0.374
Extinction correction	None	None	None	None	None	None	None

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **1**

Atom	x	y	z	U_{eq} $^{a)}$
CoA	0.5242 (1)	0.1215 (2)	0.3840 (1)	0.044
O1A	0.8079 (5)	0.1389 (4)	0.3355 (4)	0.071
O2A	0.4076 (5)	0.0046 (4)	0.5174 (4)	0.057
O3A	0.2401 (4)	0.0984 (4)	0.4280 (3)	0.058
O4A	0.6398 (5)	0.2322 (4)	0.2442 (4)	0.068
N1A	0.7149 (5)	0.0982 (5)	0.3907 (4)	0.054
N2A	0.5229 (6)	0.0351 (4)	0.4775 (5)	0.047
N3A	0.3323 (5)	0.1417 (4)	0.3752 (4)	0.047
N4A	0.5242 (6)	0.2049 (5)	0.2847 (4)	0.053
N5A	0.5483 (6)	0.2064 (4)	0.5052 (4)	0.049
C1A	0.7558 (6)	0.0426 (5)	0.4551 (5)	0.053
C2A	0.6412 (7)	0.0034 (5)	0.5046 (5)	0.052
C3A	0.2918 (6)	0.1991 (5)	0.3132 (5)	0.051
C4A	0.4047 (8)	0.2370 (5)	0.2593 (5)	0.054
C5A	0.9048 (7)	0.0223 (6)	0.4770 (6)	0.074
C6A	0.6586 (8)	−0.0652 (5)	0.5788 (6)	0.066
C7A	0.1422 (7)	0.2225 (6)	0.2936 (5)	0.070
C8A	0.3869 (9)	0.3012 (5)	0.1806 (5)	0.075
C9A	0.4861 (8)	0.0414 (6)	0.2715 (5)	0.085
C10AL	0.5926 (7)	0.0094 (6)	0.2036 (7)	0.081
C11AL	0.5254 (12)	−0.0246 (5)	0.1049 (5)	0.094
C12AL	0.5421 (16)	−0.1018 (6)	0.0817 (10)	0.104
C10AS	0.5415 (23)	0.0470 (7)	0.1662 (6)	0.101
C11AS	0.5515 (19)	−0.0356 (8)	0.1188 (10)	0.094
C12AS	0.4586 (29)	−0.0591 (14)	0.0459 (19)	0.132
C13A	0.6774 (9)	0.2503 (6)	0.5174 (6)	0.085
C14A	0.6870 (9)	0.3159 (6)	0.5947 (6)	0.079
C15A	0.6364 (9)	0.2932 (6)	0.6954 (6)	0.086
C16A	0.4979 (8)	0.2519 (6)	0.6858 (6)	0.077
C17A	0.4945 (8)	0.1870 (6)	0.6034 (5)	0.070
CoB	1.0146 (1)	0.0923 (2)	−0.1149 (1)	0.038
O1B	1.2992 (4)	0.1328 (4)	−0.0812 (4)	0.057
O2B	0.8976 (5)	−0.0321 (4)	−0.2405 (4)	0.060
O3B	0.7289 (4)	0.0575 (4)	−0.1584 (4)	0.065
O4B	1.1325 (4)	0.2195 (4)	0.0078 (4)	0.053
N1B	1.2056 (5)	0.0828 (4)	−0.1274 (4)	0.045
N2B	1.0145 (5)	0.0020 (4)	−0.2045 (4)	0.043
N3B	0.8225 (5)	0.1053 (4)	−0.1059 (4)	0.048
N4B	1.0158 (5)	0.1844 (4)	−0.0280 (4)	0.043
N5B	1.0252 (6)	0.0141 (5)	0.0163 (5)	0.058
C1B	1.2480 (6)	0.0245 (5)	−0.1860 (4)	0.044
C2B	1.1354 (6)	−0.0239 (5)	−0.2319 (5)	0.044
C3B	0.7819 (6)	0.1628 (5)	−0.0485 (4)	0.048
C4B	0.8948 (7)	0.2090 (5)	−0.0009 (5)	0.046
C5B	1.3958 (6)	0.0085 (5)	−0.2085 (6)	0.063
C6B	1.1551 (7)	−0.0892 (5)	−0.3066 (5)	0.061
C7B	0.6330 (6)	0.1826 (6)	−0.0313 (5)	0.071
C8B	0.8766 (8)	0.2779 (5)	0.0736 (5)	0.067
C9B	0.9939 (6)	0.1624 (5)	−0.2437 (5)	0.049
C10B	1.1163 (7)	0.1800 (5)	−0.3070 (6)	0.065
C11B	1.0761 (9)	0.2246 (5)	−0.4039 (6)	0.081
C12B	1.1166 (11)	0.2996 (5)	−0.4208 (9)	0.112
C13B	1.0919 (11)	0.0427 (7)	0.1103 (6)	0.106
C14B	1.1111 (10)	−0.0143 (7)	0.1972 (6)	0.088
C15B	0.9949 (14)	−0.0663 (7)	0.2150 (7)	0.123
C16B	0.9301 (10)	−0.0984 (6)	0.1198 (6)	0.089
C17B	0.9123 (9)	−0.0401 (5)	0.0312 (6)	0.075

a) $U_{\mathrm{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^{\star}a_j^{\star}\,(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **2**

Atom	x	y	z	U_{eq} $^{a)}$
Co1	0.7538 (1)	0.2470 (1)	0.2589 (1)	0.032
O1	0.5677 (3)	0.1444 (2)	0.0012 (3)	0.066
O2	1.0239 (3)	0.1593 (2)	0.4288 (3)	0.070
O3	0.9408 (2)	0.3487 (2)	0.5131 (2)	0.054
O4	0.4846 (2)	0.3308 (2)	0.0883 (3)	0.058
N1	0.6911 (3)	0.1346 (2)	0.1080 (3)	0.047
N2	0.9092 (3)	0.1416 (2)	0.3121 (3)	0.049
N3	0.8158 (3)	0.3592 (2)	0.4102 (3)	0.037
N4	0.5965 (2)	0.3498 (2)	0.2068 (3)	0.039
N5	0.8532 (2)	0.2815 (2)	0.0937 (3)	0.034
N6	1.0133 (3)	0.3306 (2)	−0.0089 (3)	0.039
C1	0.7757 (5)	0.0455 (3)	0.1059 (5)	0.060
C2	0.9050 (4)	0.0494 (3)	0.2274 (5)	0.061
C3	0.7318 (4)	0.4486 (2)	0.4076 (4)	0.044
C4	0.6027 (3)	0.4430 (2)	0.2860 (4)	0.043
C5	0.7427 (6)	−0.0511 (3)	−0.0073 (6)	0.101
C6	1.0216 (5)	−0.0420 (3)	0.2529 (7)	0.102
C7	0.7660 (5)	0.5450 (3)	0.5195 (5)	0.073
C8	0.4893 (4)	0.5342 (3)	0.2516 (5)	0.070
C9	0.6629 (4)	0.2203 (3)	0.4351 (4)	0.046
C10	0.5686 (5)	0.1435 (4)	0.4029 (5)	0.088
C11	0.5136 (4)	0.1398 (3)	0.5525 (6)	0.079
C12	0.3760 (5)	0.1623 (4)	0.5646 (8)	0.117
C13	0.9821 (3)	0.3047 (2)	0.1230 (3)	0.040
C14	0.8967 (3)	0.3229 (2)	−0.1293 (3)	0.042
C15	0.7991 (3)	0.2924 (2)	−0.0656 (3)	0.040
C16	1.1434 (3)	0.3598 (3)	−0.0152 (4)	0.053
C17	1.1663 (4)	0.3987 (4)	−0.1323 (5)	0.089

a) $U_{\mathrm{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^{\star}a_j^{\star}\,(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

the numbering of atoms are shown in Figs. 2 and 3, respectively. The crystal has two crystallographically independent molecules, A and B, which are approximately related by a pseudo inversion center. The molecule A has the disordered but-3-en-1-yl group in the ratio of 7 : 3, whereas B has the ordered group. The but-3-en-1-yl groups of A and B are surrounded by rigid cobaloxime moieties and piperidine rings.

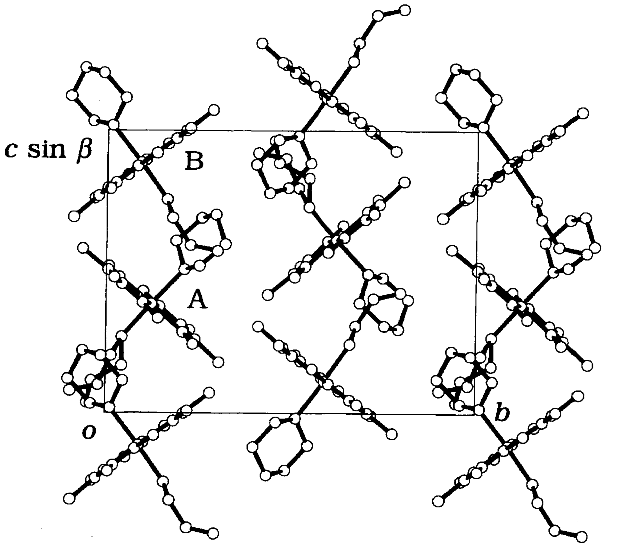


Fig. 2. Crystal structure of **1** viewed along the *a* axis.

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **3**

Atom	x	y	z	U_{eq} a)	Atom	x	y	z	U_{eq} a)
Co1	0.1199 (1)	0.2374 (1)	0.2565 (1)	0.050	C9	0.2413 (5)	0.3160 (5)	0.2782 (8)	0.086
O1	0.2492 (5)	0.1133 (5)	0.3713 (6)	0.074	C10S	0.2853 (12)	0.3609 (11)	0.1582 (10)	0.138
O2	0.0876 (5)	0.2760 (4)	−0.0293 (6)	0.080	C11S	0.3617 (10)	0.4255 (8)	0.2070 (18)	0.117
O3	−0.0040 (5)	0.3654 (4)	0.1405 (6)	0.073	C12S	0.4630 (9)	0.4126 (17)	0.1927 (34)	0.164
O4	0.1578 (6)	0.2026 (5)	0.5419 (6)	0.090	C10L	0.3166 (11)	0.3295 (12)	0.1648 (12)	0.138
N1	0.2127 (4)	0.1474 (3)	0.2536 (8)	0.058	C11L	0.4126 (7)	0.3717 (9)	0.2199 (19)	0.134
N2	0.1354 (5)	0.2268 (5)	0.0646 (6)	0.060	C12L	0.4050 (17)	0.4454 (11)	0.2808 (25)	0.147
N3	0.0313 (4)	0.3299 (3)	0.2553 (8)	0.057	N5	−0.0049 (4)	0.1544 (4)	0.2574 (9)	0.070
N4	0.1077 (5)	0.2523 (5)	0.4503 (6)	0.067	C13P	−0.0196 (13)	0.0986 (11)	0.3706 (14)	0.085
C1	0.2413 (6)	0.1194 (6)	0.1348 (9)	0.062	C14P	−0.1265 (13)	0.0585 (13)	0.3544 (23)	0.104
C2	0.1931 (6)	0.1689 (6)	0.0191 (8)	0.060	C15P	−0.1763 (15)	0.1067 (12)	0.2353 (30)	0.123
C3	0.0029 (6)	0.3582 (5)	0.3770 (9)	0.061	C16P	−0.1050 (8)	0.1812 (12)	0.2120 (28)	0.114
C4	0.0490 (6)	0.3099 (5)	0.4922 (8)	0.060	C13R	−0.0642 (17)	0.1264 (17)	0.3733 (15)	0.097
C5	0.3173 (6)	0.0525 (5)	0.1149 (10)	0.077	C14R	−0.1566 (22)	0.0771 (20)	0.3174 (23)	0.100
C6	0.2154 (8)	0.1479 (7)	−0.1291 (9)	0.087	C15R	−0.1726 (14)	0.1017 (15)	0.1660 (25)	0.093
C7	−0.0690 (7)	0.4290 (6)	0.3966 (9)	0.081	C16R	−0.0763 (13)	0.1557 (14)	0.1442 (16)	0.075
C8	0.0271 (8)	0.3289 (7)	0.6415 (9)	0.095					

a) $U_{\mathrm{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^\star a_j^\star (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **4**

Atom	x	y	z	U_{eq} a)	Atom	x	y	z	U_{eq} a)
Co1	1.4969 (3)	0.7430 (1)	0.4978 (1)	0.039	C5	1.3610 (8)	0.8312 (10)	0.1971 (9)	0.076
O1	1.4161 (7)	0.9430 (5)	0.3885 (8)	0.070	C6	1.3979 (10)	0.5689 (9)	0.2230 (10)	0.090
O2	1.4986 (6)	0.5150 (4)	0.4271 (8)	0.061	C7	1.6365 (9)	0.6544 (9)	0.7989 (8)	0.072
O3	1.5781 (7)	0.5429 (5)	0.6099 (8)	0.063	C8	1.5950 (9)	0.9193 (10)	0.7714 (9)	0.082
O4	1.4964 (7)	0.9704 (5)	0.5735 (8)	0.071	C9	1.3581 (5)	0.7054 (7)	0.5225 (6)	0.052
N1	1.4309 (7)	0.8291 (6)	0.3852 (8)	0.047	C10L	1.2975 (8)	0.7905 (9)	0.5668 (15)	0.096
N2	1.4720 (7)	0.6241 (6)	0.4007 (8)	0.049	C11L	1.2004 (10)	0.7366 (13)	0.5857 (17)	0.126
N3	1.5628 (7)	0.6557 (6)	0.6140 (8)	0.048	C12L	1.1560 (17)	0.7737 (28)	0.6581 (18)	0.213
N4	1.5201 (7)	0.8599 (6)	0.5956 (8)	0.050	C10S	1.3233 (5)	0.7524 (12)	0.6113 (7)	0.061
N5	1.6372 (6)	0.7792 (5)	0.4645 (7)	0.046	C11S	1.2247 (7)	0.6945 (11)	0.6221 (10)	0.073
N6	1.7857 (5)	0.7616 (5)	0.4210 (7)	0.054	C12S	1.1332 (6)	0.7472 (21)	0.5995 (28)	0.136
C1	1.4043 (8)	0.7732 (10)	0.2971 (9)	0.051	C13	1.6989 (6)	0.7053 (6)	0.4356 (7)	0.051
C2	0.4267 (8)	0.6516 (8)	0.3065 (10)	0.054	C14	1.6858 (7)	0.8821 (6)	0.4714 (7)	0.053
C3	1.5891 (8)	0.7089 (10)	0.6994 (9)	0.051	C15	1.7759 (6)	0.8723 (6)	0.4448 (8)	0.054
C4	1.5669 (8)	0.8316 (8)	0.6859 (9)	0.056	C16	1.8700 (7)	0.7094 (9)	0.3902 (10)	0.093

a) $U_{\mathrm{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^\star a_j^\star (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **5**

Atom	x	y	z	U_{eq} a)	Atom	x	y	z	U_{eq} a)
Co1	0.2594 (1)	0.1754 (1)	0.0785 (1)	0.033	C8	−0.1040 (4)	0.1604 (2)	0.2691 (3)	0.072
O1	0.0997 (2)	0.1812 (1)	−0.1447 (2)	0.052	C9	0.2641 (3)	0.0878 (1)	0.0690 (2)	0.053
O2	0.5640 (2)	0.1743 (1)	0.1264 (2)	0.054	C10L	0.2127 (9)	0.0593 (1)	−0.0446 (3)	0.078
O3	0.4192 (2)	0.1648 (1)	0.3021 (2)	0.056	C11L	0.2194 (6)	−0.0052 (1)	−0.0325 (4)	0.076
O4	−0.0455 (2)	0.1740 (1)	0.0306 (2)	0.059	C12L	0.3093 (9)	−0.0372 (2)	−0.0900 (8)	0.128
N1	0.2302 (2)	0.1805 (1)	−0.0877 (2)	0.039	C10S	0.2784 (11)	0.0598 (1)	−0.0481 (3)	0.063
N2	0.4522 (2)	0.1767 (1)	0.0424 (2)	0.040	C11S	0.2911 (9)	−0.0046 (1)	−0.0344 (5)	0.081
N3	0.2885 (2)	0.1671 (1)	0.2449 (2)	0.041	C12S	0.1854 (13)	−0.0401 (3)	−0.0703 (13)	0.139
N4	0.0665 (2)	0.1712 (1)	0.1144 (2)	0.043	C13	0.3590 (2)	0.2928 (1)	0.1544 (2)	0.038
N5	0.2574 (2)	0.2639 (1)	0.0884 (2)	0.034	C14	0.3638 (3)	0.3517 (1)	0.1608 (2)	0.041
C1	0.3443 (3)	0.1834 (1)	−0.1460 (2)	0.046	C15	0.2604 (3)	0.3850 (1)	0.0981 (2)	0.040
C2	0.4773 (3)	0.1813 (1)	−0.0683 (2)	0.045	C16	0.1561 (3)	0.3545 (1)	0.0290 (2)	0.044
C3	0.1737 (3)	0.1627 (1)	0.3025 (2)	0.048	C17	0.1577 (2)	0.2958 (1)	0.0263 (2)	0.040
C4	0.0418 (3)	0.1653 (1)	0.2253 (2)	0.048	C18	0.2578 (3)	0.4504 (1)	0.1034 (3)	0.058
C5	0.3378 (4)	0.1853 (2)	−0.2786 (3)	0.076	C19	0.2594 (6)	0.4743 (2)	−0.0231 (4)	0.095
C6	0.6238 (3)	0.1825 (2)	−0.1115 (3)	0.068	C20	0.3856 (4)	0.4749 (2)	0.1794 (4)	0.086
C7	0.1785 (5)	0.1555 (2)	0.4339 (3)	0.076	C21	0.1207 (4)	0.4696 (2)	0.1577 (4)	0.091

a) $U_{\mathrm{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^\star a_j^\star (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **6**

Atom	x	y	z	U_{eq} [a]
Co1	0.2434 (1)	0.0063 (1)	0.2642 (1)	0.037
P1	0.2399 (1)	0.0789 (1)	0.4096 (1)	0.035
O1	0.2200 (3)	0.2065 (3)	0.1954 (3)	0.077
O2	0.4076 (2)	−0.0969 (3)	0.3092 (2)	0.072
O3	0.2703 (2)	−0.1989 (2)	0.3152 (2)	0.066
O4	0.0818 (2)	0.1059 (3)	0.2094 (2)	0.080
N1	0.2787 (3)	0.1333 (3)	0.2239 (2)	0.049
N2	0.3679 (2)	−0.0103 (3)	0.2782 (2)	0.047
N3	0.2095 (3)	−0.1260 (3)	0.2932 (2)	0.050
N4	0.1196 (2)	0.0197 (3)	0.2402 (2)	0.054
C1	0.3632 (3)	0.1500 (4)	0.2209 (3)	0.060
C2	0.4169 (3)	0.0647 (4)	0.2541 (3)	0.059
C3	0.1248 (4)	−0.1464 (4)	0.2848 (3)	0.066
C4	0.0709 (3)	−0.0604 (5)	0.2544 (3)	0.068
C5	0.4016 (5)	0.2441 (5)	0.1830 (4)	0.112
C6	0.5173 (3)	0.0628 (6)	0.2611 (4)	0.105
C7	0.0867 (4)	−0.2489 (5)	0.3020 (4)	0.106
C8	−0.0294 (3)	−0.0620 (6)	0.2396 (4)	0.126
C9	0.2500 (3)	−0.0532 (4)	0.1419 (3)	0.060
C10L	0.2392 (9)	0.0125 (7)	0.0641 (5)	0.100
C11L	0.2386 (7)	−0.0486 (8)	−0.0194 (6)	0.082
C12L	0.3074 (7)	−0.0666 (8)	−0.0669 (6)	0.097
C10S	0.2834 (9)	0.0087 (9)	0.0677 (6)	0.057
C11S	0.2798 (12)	−0.0574 (13)	−0.0137 (9)	0.096
C12S	0.2267 (15)	−0.0420 (19)	−0.0841 (10)	0.174
C13	0.3371 (3)	0.1616 (3)	0.4306 (2)	0.042
C14	0.3411 (3)	0.2564 (4)	0.3930 (3)	0.062
C15	0.4189 (4)	0.3147 (5)	0.4032 (4)	0.091
C16	0.4933 (4)	0.2750 (6)	0.4497 (4)	0.095
C17	0.4909 (3)	0.1817 (5)	0.4847 (3)	0.075
C18	0.4135 (3)	0.1240 (4)	0.4764 (3)	0.053
C19	0.1396 (2)	0.1526 (3)	0.4300 (2)	0.038
C20	0.0594 (3)	0.0995 (4)	0.4235 (3)	0.058
C21	−0.0209 (3)	0.1451 (5)	0.4404 (3)	0.072
C22	−0.0216 (4)	0.2441 (5)	0.4661 (4)	0.079
C23	0.0566 (4)	0.2967 (4)	0.4759 (4)	0.089
C24	0.1379 (3)	0.2510 (4)	0.4586 (3)	0.066
C25	0.2467 (2)	−0.0001 (3)	0.5086 (2)	0.039
C26	0.2638 (3)	−0.1022 (3)	0.5062 (3)	0.049
C27	0.2708 (3)	−0.1578 (4)	0.5835 (3)	0.061
C28	0.2604 (3)	−0.1125 (4)	0.6623 (3)	0.065
C29	0.2439 (3)	−0.0098 (4)	0.6655 (3)	0.064
C30	0.2356 (3)	0.0466 (4)	0.5899 (3)	0.052

a) $U_{\mathrm{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^{*}a_j^{*}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

Table 8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of **7**

Atom	x	y	z	U_{eq} [a]
Co1	1.2611 (1)	0.7756 (1)	0.0420 (1)	0.033
O1	1.0309 (2)	0.7528 (2)	−0.1915 (3)	0.050
O2	1.4001 (3)	0.5938 (2)	0.1553 (3)	0.059
O3	1.4969 (2)	0.7974 (3)	0.2666 (3)	0.059
O4	1.1287 (2)	0.9569 (2)	−0.0805 (3)	0.049
N1	1.1195 (2)	0.6954 (2)	−0.1105 (3)	0.039
N2	1.2966 (3)	0.6197 (2)	0.0562 (3)	0.043
N3	1.4064 (2)	0.8541 (2)	0.1878 (3)	0.040
N4	1.2298 (2)	0.9308 (2)	0.0215 (3)	0.037
N5	1.1615 (2)	0.8109 (2)	0.2295 (3)	0.035
N6	1.0004 (2)	0.8488 (2)	0.3622 (3)	0.038
C1	1.1123 (3)	0.5797 (3)	−0.1347 (4)	0.047
C2	1.2174 (4)	0.5350 (3)	−0.0360 (4)	0.050
C3	1.4171 (3)	0.9691 (3)	0.2093 (4)	0.042
C4	1.3116 (3)	1.0140 (3)	0.1107 (4)	0.040
C5	1.0088 (4)	0.5010 (4)	−0.2536 (5)	0.075
C6	1.2358 (5)	0.4061 (3)	−0.0445 (6)	0.080
C7	1.5270 (4)	1.0439 (4)	0.3138 (5)	0.064
C8	1.2983 (4)	1.1418 (3)	0.1098 (5)	0.059
C9	1.3554 (4)	0.7417 (3)	−0.1518 (4)	0.054
C10L	1.3801 (5)	0.6174 (4)	−0.2447 (5)	0.054
C11L	1.3113 (5)	0.5542 (4)	−0.3939 (6)	0.061
C12L	1.3466 (7)	0.4308 (5)	−0.4866 (9)	0.090
C10S	1.3318 (23)	0.6417 (11)	−0.3058 (19)	0.095
C11S	1.3754 (17)	0.5285 (10)	−0.3404 (19)	0.061
C12S	1.3051 (28)	0.4277 (15)	−0.4784 (32)	0.090
C13	1.0445 (3)	0.8512 (3)	0.2270 (4)	0.038
C14	1.0964 (3)	0.8051 (3)	0.4567 (4)	0.043
C15	1.1947 (3)	0.7830 (3)	0.3746 (4)	0.042
C16	0.8757 (3)	0.8814 (3)	0.3923 (4)	0.050
C17	0.8284 (4)	0.8660 (4)	0.5114 (5)	0.068

a) $U_{\mathrm{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^{*}a_j^{*}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

(But-3-en-1-yl)(1-vinylimidazole)cobaloxime 2: The crystal structure viewed along the *b* axis and the molecular structure are shown in Figs. 4 and 5. respectively. Two but-3-en-1-yl groups, which take ordered structures, are in close contact around an inversion center at (0.5, 0, 0.5) and a pair of the groups are surrounded by the cobaloxime moieties and the 1-vinylimidazole ligands.

(But-3-en-1-yl)(pyrrolidine)cobaloxime 3: The crystal structure viewed along the *c* axis and the molecular structure are shown in Figs. 6 and 7, respectively. The crystal structure is similar to that of **1**, although the crystal system is different from **1**. Each alkenyl group is isolated from the neighboring alkenyl group by the cobaloxime moieties and the disordered pyrrolidine rings. The molecule has a disordered but-3-en-1-yl group with a ratio of 1 : 1. The pyrrolidine ligand also has a disordered structure around the Co–N5 bond with a ratio of 6 : 4.

(But-3-en-1-yl)(1-methylimidazole)cobaloxime 4. Figures 8 and 9 show the crystal structure viewed along the *b* axis and the molecular structure, respectively. The but-3-en-1-yl group is disordered in the ratio of 6 : 4 and is surrounded by the glyoxime moieties and the 1-methylimidazole ligands.

(But-3-en-1-yl)(4-*t*-butylpyridine)cobaloxime 5. The crystal structure viewed along the *a* axis and the molecular structure are shown in Figs. 10 and 11, respectively. The but-3-en-1-yl group is disordered in the ratio of 6 : 4. The two but-3-en-1-yl groups face to each other around an inversion center with the shortest contact of 3.93 Å and the pairs of the alkyl groups are stacked along the *a* axis.

(But-3-en-1-yl)(triphenylphosphine)cobaloxime 6. The crystal structure viewed along the *a* axis and the molecular structure are shown in Figs. 12 and 13, respectively. The but-3-en-1-yl group is disordered in the ratio of 6 : 4. The two alkenyl groups face to each other around an inversion

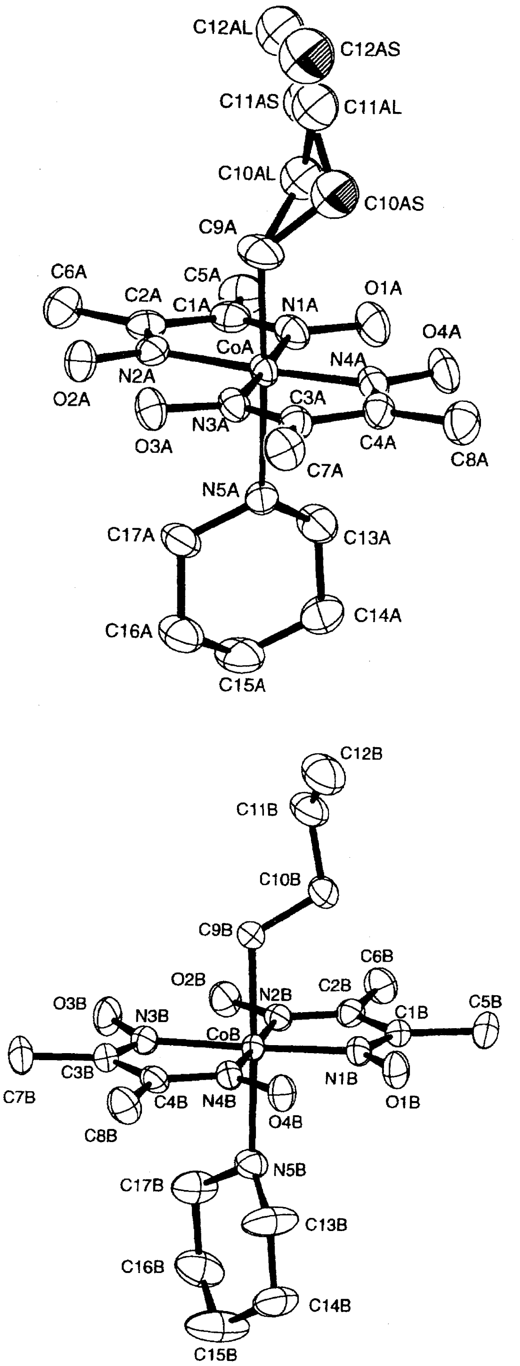


Fig. 3. Molecular structure of molecule A (above) and molecule B (below) of **1** and numbering scheme of the atoms. The thermal ellipsoids show at 30% probability level. The atomic displacement parameters of the disordered 3-butenyl groups were refined isotropically and one of the disordered parts was discribed by shaded octants (same as above for the following Figs.).

center. The pairs of the alkenyl groups are stacked along the *a* axis.

(But-2-en-1-yl)(1-methylimidazole)cobaloxime 7. Figures 14 and 15 show crystal structure viewed along the *b* axis and the molecular structure, respectively. The but-2-en-1-yl group is disordered in the ratio of 1 : 1 and its conformation

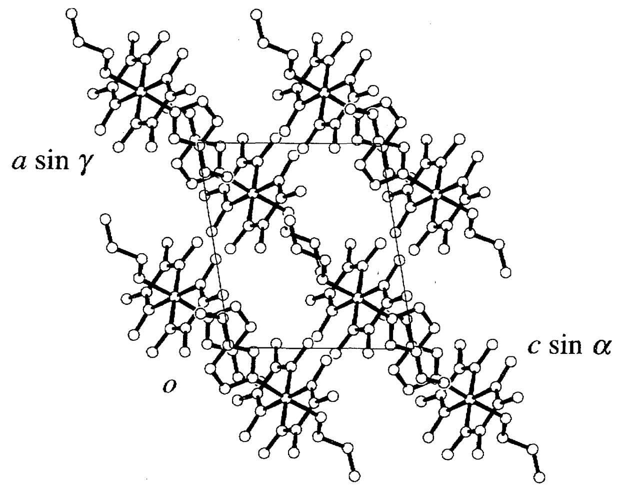


Fig. 4. Crystal structure of **2** viewed along the *b* axis.

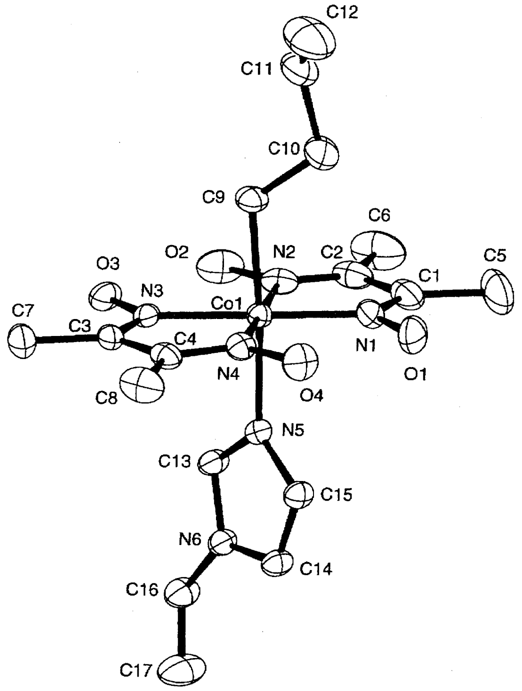


Fig. 5. Molecular structure of **2** and numbering scheme of the atoms. The thermal ellipsoids show at 30% probability level.

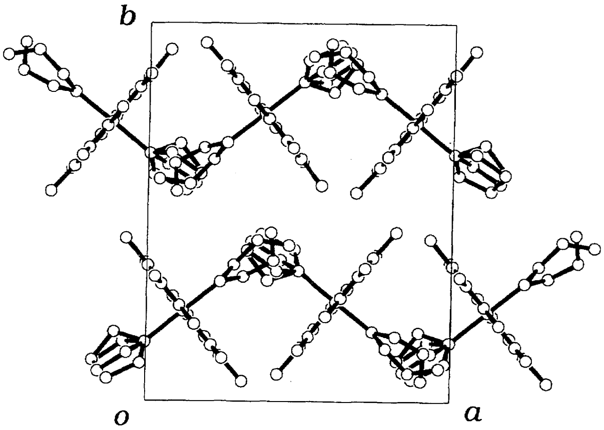


Fig. 6. Crystal structure of **3** viewed along the *c* axis.

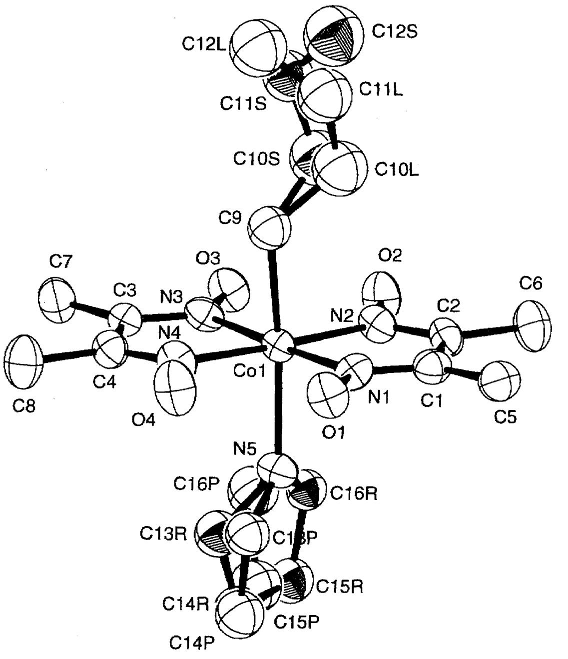


Fig. 7. Molecular structure of **3** and numbering scheme of the atoms. The thermal ellipsoids show at 30% probability level.

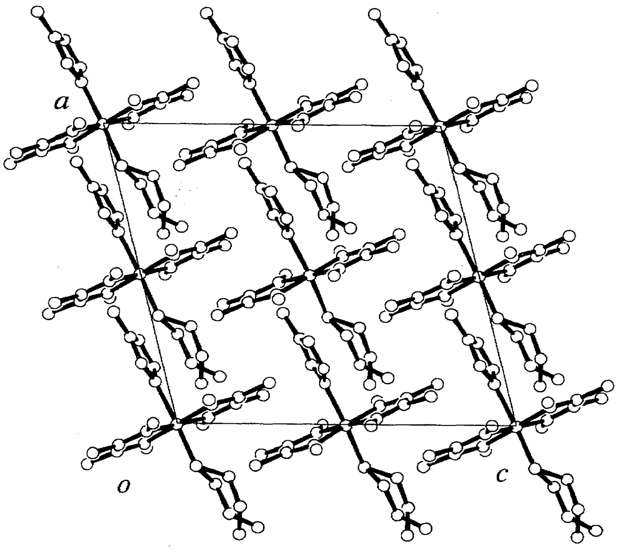


Fig. 8. Crystal structure of **4** viewed along the *b* axis.

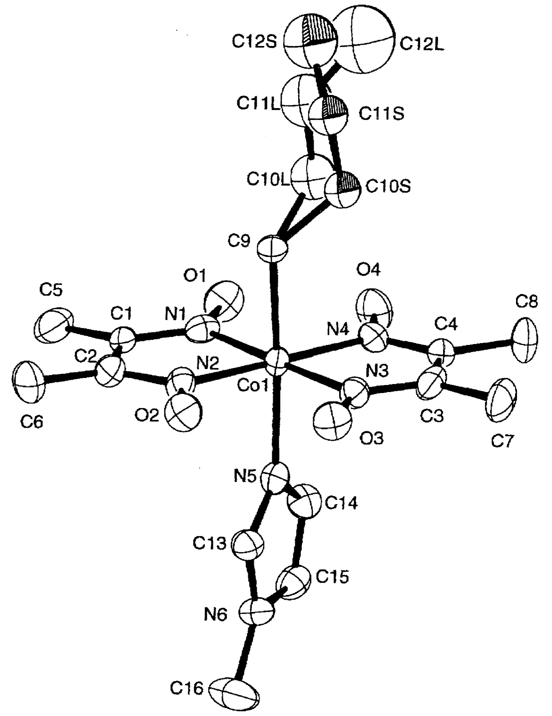


Fig. 9. Molecular structure of **4** and numbering scheme of the atoms. The thermal ellipsoids show at 30% probability level.

is *trans*. Although **7** and **2** have the same space group and their molecular structures are different only in the positions of the double bonds, the molecular arrangements are different. This may indicate that **2** is not so easily changed to **7** without destroying the single crystal form.

Discussion

The structures indicate that the but-3-en-1-yl group tends to have disordered structures. The torsion angles of the but-3-en-1-yl group are summarized in Table 9, in which the occupancy factors of the disordered groups are also given. The angles of Co–C9–C10–C11 range from 153.8(10)° to 180.0(8)°, which means the but-3-en-1-yl group takes a perpendicular conformation to the cobaloxime plane.

When the powdered sample of the (but-3-en-1-yl)cobalox-

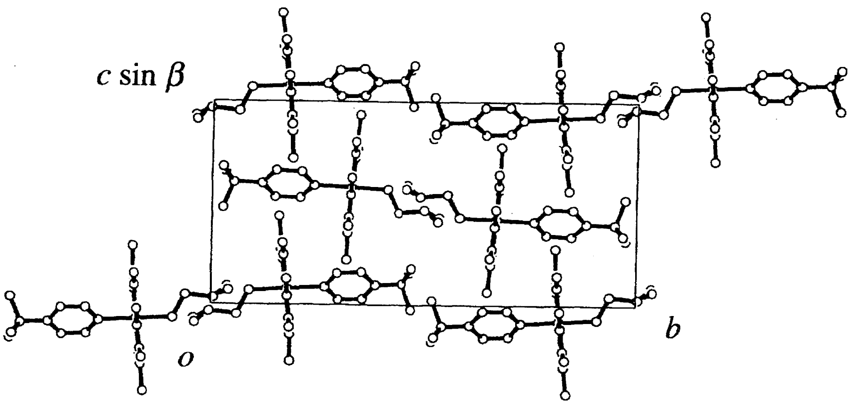


Fig. 10. Crystal structure of **5** viewed along the *a* axis.

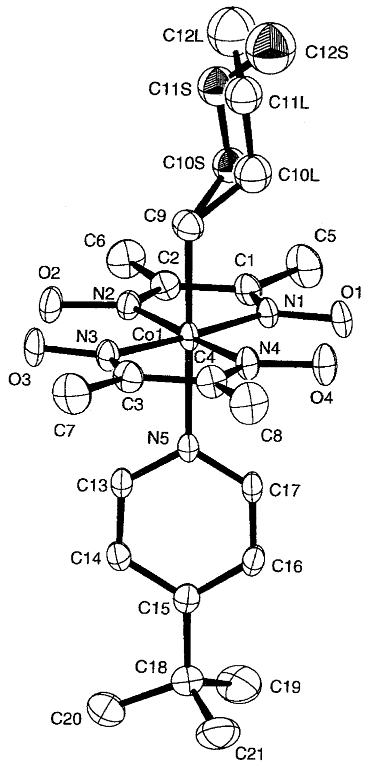


Fig. 11. Molecular structure of **5** and numbering scheme of the atoms. The thermal ellipsoids show at 30% probability level.

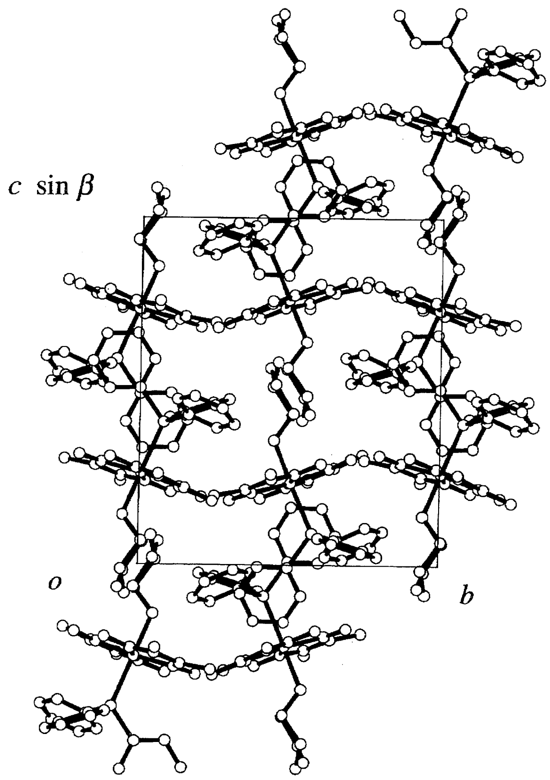


Fig. 12. Crystal structure of **6** viewed along the *a* axis.

ime is isomerized to the (but-2-en-1-yl)cobaloxime as shown in the Scheme 1, the reaction would proceed via migration of

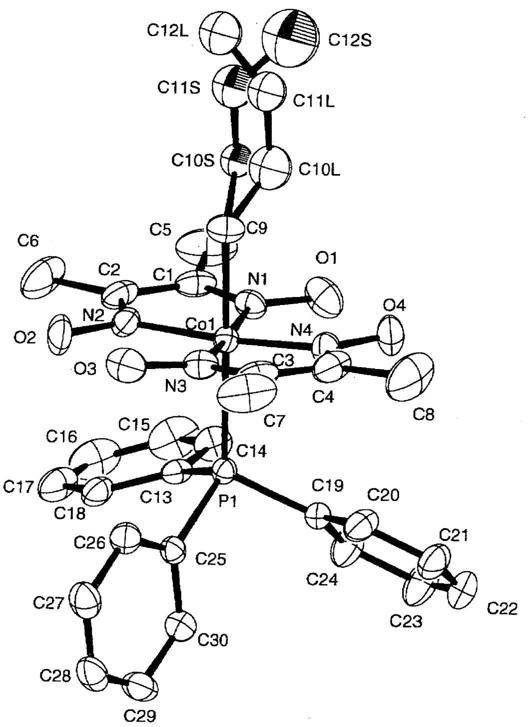


Fig. 13. Molecular structure of **6** and numbering scheme of the atoms. The thermal ellipsoids show at 30% probability level.

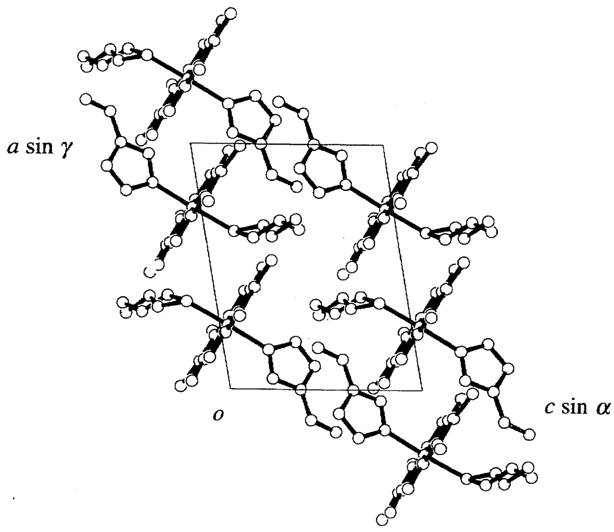


Fig. 14. Crystal structure of **7** viewed along the *b* axis.

one of the two hydrogen atoms bonded to the C10 atoms to C12 in the but-3-en-1-yl group. This causes migration of the double bond of C11=C12 to C10=C11. The distance between the cobalt atom and the nearest hydrogen atom bonded to C10 in the six complexes are within a range of 3.1—3.3 Å. The neutron diffraction analysis of the (1-cyanoethyl)cobaloxime complex showed that the photoinduced hydrogen exchange takes place between hydrogen atoms which are separated within 3.3 Å from the cobalt atom.[11] The fact suggests that the migration of the hydrogen atom would be assisted by the cobalt atom.

The conformation and disordered structure of the but-3-

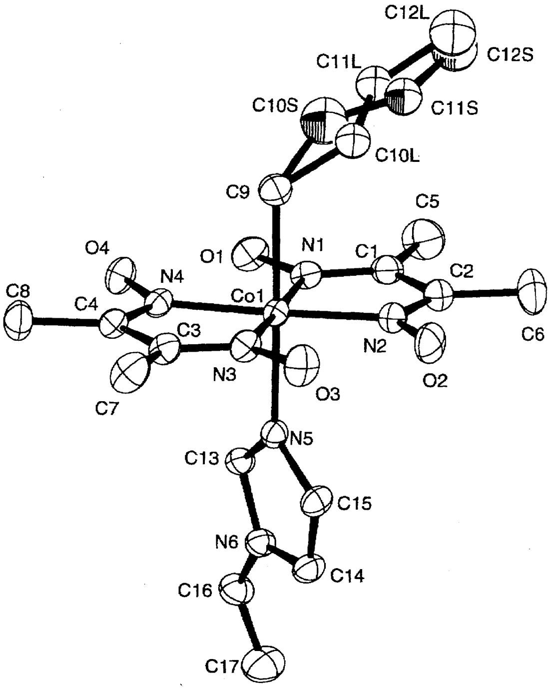


Fig. 15. Molecular structure of **7** and numbering scheme of the atoms. The thermal ellipsoids show at 30% probability level.

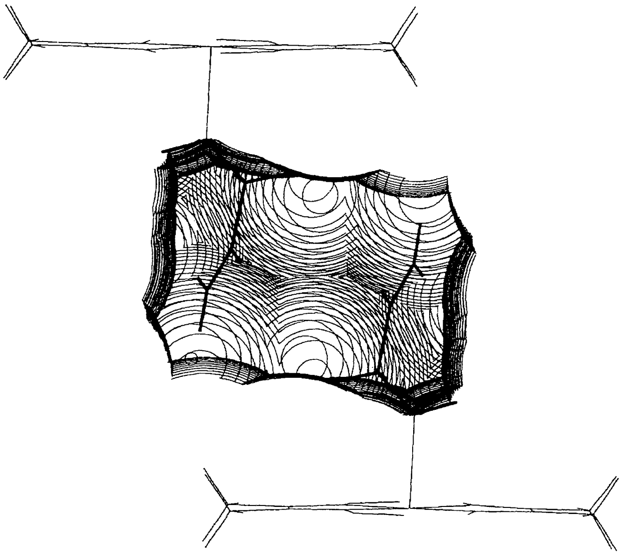


Fig. 16. The reaction cavity of **2**. Two reactive groups related with an inversion center were closely packed and surrounded by rigid cobaloxime planes and vinylimidazole moieties.

en-1-yl group are very similar to those of (aqua)(3-methylbut-3-en-1-yl)bis[(2-pyridinecarboxamido)benzene]cobaloxime.[21] No interaction between the C=C double bond and the Co atom was observed in all the molecular structures. Therefore the formation of the (cyclopropylmethyl)cobaloxime and following rearrangement of the carbon skeleton is not likely to happen in the solid state.[13]

Although the isomerization of the (but-3-en-1-yl)cobaloxime is simpler than the 2-1 isomerization of the 2-cyanoethyl group, it needs a geometrical change for the but-3-en-1-yl group to be transformed to the but-2-en-1-yl group. Actually, the conformation of the but-2-en-1-yl group in **7** is quite different from that of the but-3-en-1-yl group in **2**. Such a large conformational change is not likely to happen without destroying the single crystal form.

In order to examine the relationship between the reactivity and the crystal structure, the reaction cavity for the but-3-en-1-yl group in each crystal was calculated in the same way as that reported previously.[22] For the crystals **2**, **5**, and **6**, the combined cavity was also calculated for a pair of the but-3-en-1-yl groups around an inversion center, since those reactive groups are in contact with each other around an inversion center. The cavity volume per a reactive group is obtained by dividing the combined cavity into two. On the other hand, the cavity volumes of **1**, **3**, and **4** are the same as those calculated in the usual way, since the but-3-en-1-yl groups in those crystals are isolated from the neighboring reactive groups. Table 10 lists the cavity volume for each crystal. The cavity of the A molecule in the crystal **1** has significantly greater volume than that of B. This well explains the reason why only A takes a disordered structure. Both of the cavities of the A and B molecules in crystal **3** have enough size to

Table 9. Torsion Angles and Occupancies of (But-3-en-1-yl)cobaloxime Complexes

Complex		Part	Co–C9–C10–C11	C9–C10–C11–C12	Occupancy
1	Molecule 1	L	−159.4(7)	−119.7(13)	0.63(2)
		S	153.8(10)	103.7(18)	0.37(2)
	Molecule 2		173.7(6)	114.3(9)	1.0
2			−179.1(3)	118.0(5)	1.0
3		L	−164.9(9)	−59.2(22)	0.56(2)
		S	170.3(9)	104.9(23)	0.44(2)
4		L	−175.1(13)	152.3(30)	0.52(2)
		S	−170.0(8)	−107.5(23)	0.48(2)
5		L	−177.8(3)	−112.6(7)	0.58(1)
		S	178.4(4)	107.6(10)	0.42(1)
6		L	−175.1(6)	−95.6(14)	0.61(1)
		S	−180.0(8)	113.7(24)	0.39(1)
7		L	100.5(5)	176.0(5)	0.79(1)
		S	−84.3(27)	156.1(24)	0.21(1)

Table 10. Reaction Rate and Volume of Reaction Cavity

Crystal		Reaction rate $\times 10^{-2}$ h^{-1}	Volume of reaction cavity (Å^3)	Combined cavity for a reactive group[a]
1	Molecule A	0.5	19.9	
	Molecule B		16.1	
2		0.8	25.1	33.5
3	Disorder P[b]	1.1	21.0	
	Disorder R[b]		18.5	
4		1.4	25.4	
5		3.2	32.8	42.2
6		3.3	23.6	22.5

a) Since the cavity is shared by some but-3-enyl groups, the whole cavity was divided by the number of the but-3-enyl groups into the volume described here. b) Only a disordered structure P (or R) of the pyrrolidine ring was included for the calculation of the reaction cavity.

take the disordered structure.

For the isolated cavities of the crystals **1**, **3**, and **4**, the greater cavity shows the greater reaction rate, but the reaction rates of the crystals are significantly smaller than those of the crystals **5** and **6**, in which a pair of the reactive groups face to each other around an inversion center. This suggests that the cooperative motion of the reactive group would play an important role in the isomerization process. In the crystal **2**, on the other hand, a pair of reactive groups is situated around an inversion center. However, the pair is in a cage made by cobaloxime moieties and axial base ligands as shown in Fig. 4. The combined cavity is shown in Fig. 16. On the other hand, the pair observed in the crystal **5** or **6** makes a column structure along the *a* axis as shown in Figs. 10 and 12, respectively. Such a column structure would enhance the cooperative motion and show a greater reaction rate than that of the isolated reactive group.

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