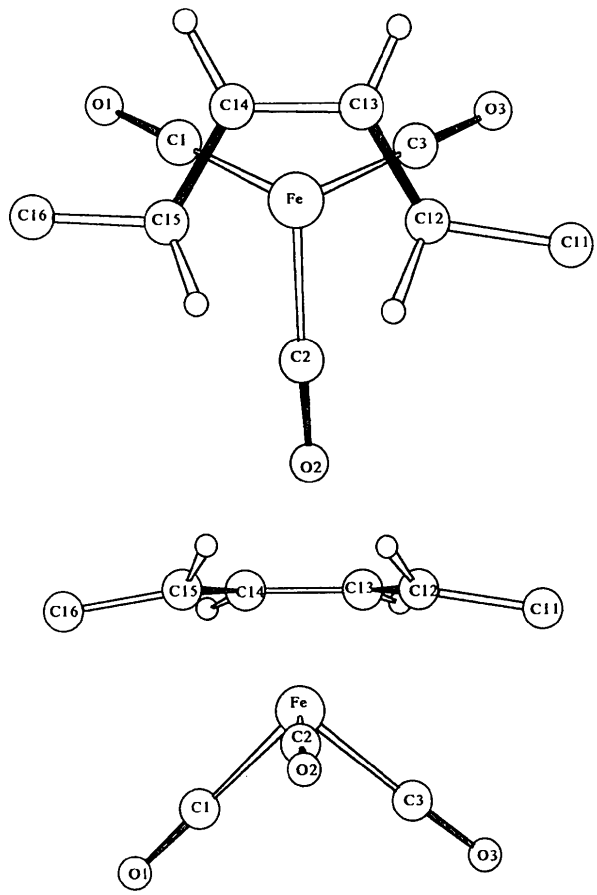

Fig. 4. Perpendicular and planar view of the butadienetricarbonyliron moiety.

Discussion. Table 1 contains crystal and refinement data for (1), (2) and (3), while Tables 2, 3 and 4 give the atomic positional parameters and B_{eq} values for the non-H atoms of the three compounds. Table 5 presents selected bond distances and Table 6 selected valence angles. Figs. 1, 2(*a*), 2(*b*) and 3 are *ORTEP* (Johnson, 1965) drawings of the three molecules. As can be seen from Tables 5 and 6, the three geometries are homogeneous, in particular for (1) and (2). In the butadiene–tricarbonyliron moiety, the two H atoms (H12 and H15) lie above the C12—C13—C14—C15 plane as shown in Fig. 4. The hybridization of the corresponding C atoms (C12 and C15) is intermediate between sp^3 and sp^2 as a result of complexation by the tricarbonyliron moiety (Messager & Toupet, 1986). With regard to the stereochemical outcome of this synthesis, in each case the first step of the reaction (the osmylation of the double bonds) occurs *anti* to the Fe(CO)$_3$ moiety. Thus, these results not only indicate the stereochemistry of the three compounds, but also show that stereocontrolled preparation of other natural product derivatives in this family is possible.

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Acta Cryst. (1991). C**47**, 1177–1180

β–α Photoisomerization of Cobaloxime Complexes in the Solid State. II. A Topochemically Controlled Reaction

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(*Received* 27 *August* 1990; *accepted* 2 *January* 1991)

Abstract. (β-Cyanoethyl)bis(dimethylglyoximato)(pyridine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), [Co(C$_3$H$_4$N)(C$_4$H$_7$N$_2$O$_2$)$_2$(C$_5$H$_5$N)], crystallizes in two forms. The rates of β–α isomerization by exposure to visible light differ for the two forms. One of the two forms, form I, has been reported previously [Zangrando, Bresciani-Pahor, Randaccio, Charland & Marzilli (1986).

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Organometallics, **5**, 1938–1944]. In order to compare the structures of the two forms, the structure of the other form, form II, was determined. $M_r = 422·33$, monoclinic, $C2/c$, $a = 28·686$ (6), $b = 7·608$ (1), $c = 18·006$ (9) Å, $\beta = 104·85$ (2)°, $V = 3798$ (2) Å^3, $D_x = 1·478$ g cm^{-3}, $Z = 8$, $T = 298$ K, $F(000) = 1760$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 8·78 cm^{-1}, $R = 0·064$ for 2747 observed reflections. The reactive β-cyanoethyl groups in forms I and II have significantly different conformations, which explains the different reaction rates from the topochemical point of view.

Introduction. The β-cyanoethyl group is isomerized to the α-cyanoethyl group when the powdered samples of (β-cyanoethyl)cobaloxime complexes [cobaloxime = bis(dimethylglyoximato)cobalt(III)] are exposed to visible light (Ohgo & Takeuchi, 1985). In a previous paper we described the β–α isomerization of (β-cyanoethyl)(3-methylpyridine)cobaloxime (β-3mepy complex) (Uchida, Danno, Sasada & Ohashi, 1987). The β-3mepy complex crystallizes in two crystalline forms, and the isomerization rates of the two forms are different. The difference is explained on the basis of the reaction cavity (Ohashi, Uchida, Sasada & Ohgo, 1983), *i.e.* the free space around the reactive group. It has been found that (β-cyanoethyl)cobaloxime with pyridine as an axial base ligand (β-py complex) also crystallizes in two forms and the isomerization rates are different. Structure analysis shows that there should be another factor controlling the reaction rate. This paper reports a new factor in the β-α isomerization.

Experimental. The title complex was synthesized in the same way as reported previously (Schrauzer & Windgassen, 1967). Forms I and II were obtained separately when hot methanol solutions were cooled slowly and quickly, respectively.

Form II: orange–yellow needles, systematic absences $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, crystal size 0·1 × 0·1 × 0·4 mm, Rigaku AFC-4 diffractometer. Mo $K\alpha$ monochromated by graphite, unit-cell dimensions from 2θ values of 18 reflections in the range $16 < 2\theta < 28°$, intensities measured up to $2\theta = 50°$. Range of hkl −34 to 32, 0 to 9 and 0 to 21, $\omega/2\theta$ scan mode, scan rate 4°(θ) min^{-1}, scan width $(1·0 + 0·35\tan\theta)°$, stationary background counts accumulated for 5 s before and after each scan, no significant variation of intensity in three standard reflections. 3338 reflections, of which 2747 with $|F_o| > 3\sigma(|F_o|)$ for structure determination. Lorentz and polarization corrections and no absorption correction.

Table 1. *Final atomic coordinates* (× 10^5 *for* Co; × 10^4 *for* C, N *and* O) *and equivalent isotropic thermal parameters* (Å^2) *for form* II

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

	x	y	z	B_{eq}
Co	39463 (2)	16084 (8)	10564 (4)	2·2
N(1)	4484 (1)	2557 (5)	780 (2)	2·7
N(2)	4370 (1)	−308 (5)	1334 (2)	2·6
N(3)	3414 (1)	692 (5)	1362 (2)	2·7
N(4)	3521 (1)	3528 (5)	790 (2)	2·8
O(1)	4491 (1)	4205 (5)	493 (2)	3·9
O(2)	4248 (1)	−1772 (4)	1651 (2)	3·7
O(3)	3418 (1)	−914 (5)	1694 (2)	3·9
O(4)	3647 (1)	5003 (4)	479 (2)	3·8
C(1)	4864 (2)	1559 (7)	880 (3)	2·9
C(2)	4798 (2)	−142 (6)	1209 (3)	2·8
C(3)	3031 (2)	1668 (7)	1247 (3)	3·2
C(4)	3093 (2)	3355 (7)	908 (3)	3·2
C(5)	5317 (2)	2165 (9)	698 (4)	4·1
C(6)	5170 (2)	−1560 (10)	1390 (4)	4·7
C(7)	2580 (2)	1130 (11)	1445 (4)	5·3
C(8)	2729 (3)	4808 (10)	733 (5)	5·4
N(5)	3689 (1)	564 (5)	−27 (2)	2·5
C(9)	3569 (2)	−1156 (6)	−112 (3)	2·7
C(10)	3408 (2)	−1920 (7)	−824 (3)	3·4
C(11)	3368 (2)	−913 (8)	−1481 (3)	3·8
C(12)	3483 (2)	831 (8)	−1395 (3)	3·6
C(13)	3642 (2)	1522 (7)	−671 (3)	3·0
C(14)	4232 (2)	2475 (7)	2127 (3)	3·1
C(15)	4178 (3)	4400 (7)	2316 (4)	4·4
C(16)	3730 (3)	4800 (7)	2519 (4)	5·2
N(6)	3386 (3)	5077 (8)	2690 (4)	7·7

Structure solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976), positions of all H atoms obtained from a difference map. C—H distances constrained to be 1·00 Å, anisotropic and isotropic thermal parameters for the non-H atoms and for H atoms, respectively. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma(|F_o|)^2 + 0·000365(|F_o|)^2]^{-1}$, $(\Delta/\sigma)_{\max} = 0·1$, $\Delta\rho_{\max} = 0·5$ e Å^{-3}, $R = 0·064$, $wR = 0·054$ and $S = 2·72$ for 2747 reflections. The atomic parameters for the non-H atoms are given in Table 1.* Atomic scattering factors including the anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculation was carried out on a FACOM-HITAC system M-270H computer at Tokyo Institute of Technology.

The structure of form I was also determined independently. Since the thermal ellipsoids of the atoms of the cyanoethyl group were very oblate, we assumed a disordered structure for the cyanoethyl group. Although our results seem reasonable for the structure of the cyanoethyl group, the rest of the structure is almost the same as reported previously (Zangrando, Bresciani-Pahor, Randaccio, Charland & Marzilli, 1986).

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* Lists of anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond distances and angles and structure factors for form II have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53781 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Isomerization rates were measured by the same method as reported previously (Uchida *et al.*, 1987).

Discussion. The crystal structure of form II is shown in Fig. 1. There are a few short contacts in the structure [O(4)—C(9^{i}), 3·099 (6) and C(15)—O(2^{i}), 3·174 (8) Å (i: x, $1+y$, z)], but no short contacts between the reactive cyanoethyl groups.

The molecular structure in form II with the atom-numbering scheme is shown in Fig. 2. Selected bond distances and angles and torsion angles around Co—C, Co—N and C(14)—C(15) bonds are listed in Table 2. The significant difference in the two molecular structures of the forms I and II is the conformation of the cyanoethyl groups. The cyanoethyl group in form I takes a nearly perpendicular conformation to the cobaloxime plane, while that in form II is almost parallel to the plane.

The conversion curves for the β–α isomerization of forms I and II are shown in Fig. 3. The reaction rate of form II is greater than that of form I. It has been found that there is a positive correlation between reaction rates and the cavity volumes for the cyanoethyl groups in the isomerization of the two forms of the β-3mepy complex (Uchida *et al.*, 1987). The cavity volumes for the cyanoethyl groups in the two forms I and II were calculated to be 12·31 and 10·51 Å^3, respectively. Form II has a greater reaction rate but smaller cavity than form I. This seems to indicate that simple comparison of the cavity size may be inadequate when the cyanoethyl groups have

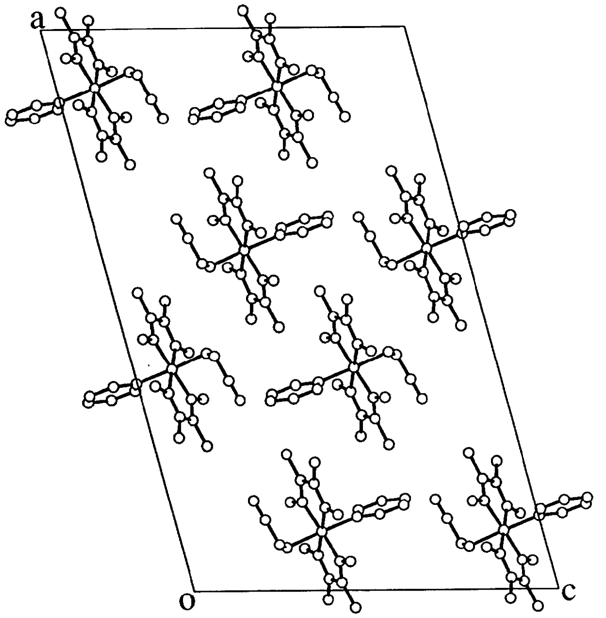

Fig. 1. Crystal structure of form II viewed along the *b* axis.

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *for form* II

Co—N(1)	1·881 (4)	Co—N(4)	1·884 (4)
Co—N(2)	1·882 (4)	Co—N(5)	2·060 (4)
Co—N(3)	1·884 (4)	Co—C(14)	2·003 (5)
N(1)—Co—N(2)	81·4 (2)	N(2)—Co—N(3)	98·8 (2)
N(3)—Co—N(4)	80·9 (2)	N(1)—Co—N(5)	90·9 (2)
N(1)—Co—N(4)	99·0 (2)	N(1)—Co—C(14)	88·2 (2)
N(1)—Co—C(14)—C(15)	79·5 (5)	Co—C(14)—C(15)—C(16)	85·8 (7)
N(1)—Co—N(5)—C(9)	128·1 (4)		

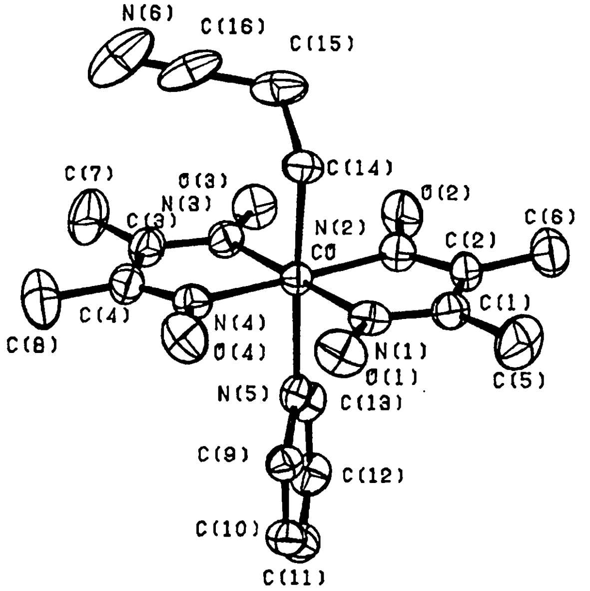

Fig. 2. *ORTEP* (Johnson, 1965) drawing of form II with the atom-numbering scheme. Thermal ellipsoids are shown at the 50% probability level.

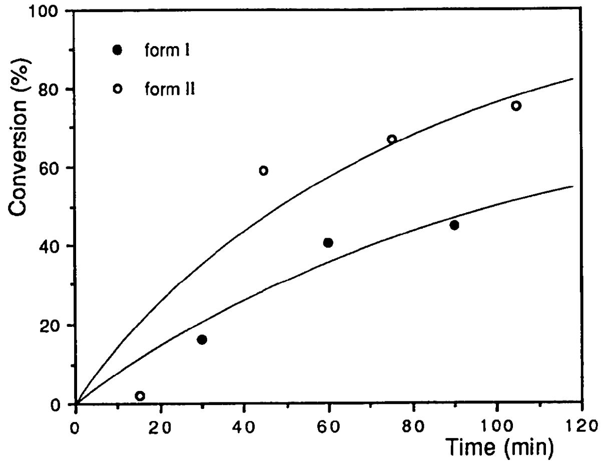

Fig. 3. Conversion curves for β–α isomerization of forms I and II. Approximate first-order reaction curves are obtained by least-squares fitting. The rate constants are $1·2 \times 10^{-4}$ s^{-1} for form I and $2·4 \times 10^{-4}$ s^{-1} for form II.

quite different conformations as observed in these two forms. The α-cyanoethyl group of [(*S*)-1-cyanoethyl](pyridine)cobaloxime (α-py complex) (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982), which is a product of the β–α isomerization, is nearly parallel to the cobaloxime plane. The cyanoethyl group in form II bears closer resemblance in shape to that of the α-py complex than that in form I. This means that the atoms of the cyanoethyl group in form II move to a smaller extent than those in form I in β–α isomerization. The topochemical rule (Cohen & Schmidt, 1964) should be applicable when the reactive groups have such different conformations. This factor, the second factor, appears to control the reaction rate, in preference to the cavity size (the first factor), in the case of significantly different conformers of the reactive group.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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Acta Cryst. (1991). C**47**, 1180–1183

Structure of *cis*-Dichlorobis(3,5-diphenylpyrazole)platinum(II) Tetrahydrofuran Solvate: a Platinum Complex Containing Two Pyrazole Ligands

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(*Received* 2 *August* 1990; *accepted* 13 *November* 1990)

Abstract. $[PtCl_2(C_{15}H_{12}N_2)_2].C_4H_8O$, $M_r = 778{\cdot}7$, triclinic, $P\bar{1}$, $a = 9{\cdot}954\ (3)$, $b = 11{\cdot}579\ (3)$, $c = 15{\cdot}141\ (3)$ Å, $\alpha = 70{\cdot}30\ (2)$, $\beta = 75{\cdot}79\ (2)$, $\gamma = 78{\cdot}54\ (2)^\circ$, $V = 1579{\cdot}8\ (7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}637$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 4{\cdot}69$ mm^{-1}, $F(000) = 767{\cdot}8$, $T = 298$ K. The structure consists of a square-planar platinum(II) complex containing two chloride and two 3,5-diphenylpyrazole ligands in *cis* geometry along with an interstitial molecule of tetrahydrofuran. Convergence to final conventional R values of $R = 0{\cdot}0388$ and $wR = 0{\cdot}0406$ was obtained using 331 variable parameters and 3476 reflections with $F_o^2 > 3\sigma(F_o^2)$.

Introduction. Heterometallic doubly bridged complexes can be formed in a stepwise fashion from mononuclear compounds which contain two dangling ligands. Such compounds can be thought of as metal-containing ligands.

Focusing our attention on the heavier metals, we have synthesized the mononuclear complex $[Au\{(CH_2)P(C_6H_5)_2S)\}_2]$ containing two dangling S atoms. Using this as starting material, we have synthesized and structurally characterized some mixed metal complexes such as the ones containing AuPtAu (Murray, Briggs, Garzòn, Raptis, Porter & Fackler, 1987), AuTl (Wang, Fackler, King & Wang, 1988), AuPbAu (Wang, Garzòn, King, Wang & Fackler, 1989) and AuHg (Wang & Fackler, 1988) metal cores. We are extending these studies to complexes involving 3,5-diphenylpyrazole ligands.

Some transition-metal complexes of the general types $L_2M(pz)_2$, $L_2M(pzH)_2$, $L_2M[3,5\text{-}(CH_3)_2pz]$ and $L_2M[3,5\text{-}(CH_3)_2pzH]_2$, where L = Lewis base, M = Pt, Pd, pz = pyrazolato anion ($C_3H_3N_2$) and pzH = pyrazole ($C_3H_4N_2$), are known (Bonati & Clark,

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0108-2701/91/061180-04$03.00