Solid State Unidirectional Photoisomerization of (β-Substituted Ethyl)bis(disubstituted Glyoximato)(L)cobalt(III) to the α-Substituted Ethyl Complexes (L = Pyridine or Primary Amine)

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Photoisomerization of β-cyanoethyl- and β-(methoxycarbonyl)ethyl-bis(disubstituted glyoximato)(L)cobalt(III) (L = pyridine or primary amines) to the α-substituted ethyl complexes occurred in the solid state, but the reverse (α →β) isomerization was not observed, despite the fact that Co–C bond cleavage occurred.

Although solid state reactions of organic compounds are well documented,[1] organometallic solid state reactions have rarely been studied.[2,3] To our knowledge, reactions accompanying a genuine rearrangement of chemical bonds have not been reported so far in this field.

We now report that isomerization of (β-substituted ethyl)-bis(disubstituted glyoximato)(L)cobalt(III) (L = pyridine or primary amine) to the α-substituted ethyl complexes occurs on visible light irradiation of the sample in the solid state and the reverse (α → β) isomerization does not proceed.

When a 1% KBr disk of (β-cyanoethyl)bis-(dimethylglyoximato)(pyridine)cobalt(III) was irradiated with sunlight or a sun lamp, the absorption intensity at 2237 cm^{-1} (v_{CN} of the β-cyanoethyl complex) decreased and that at 2204 cm^{-1} (v_{CN} of the α-cyanoethyl complex) increased with irradiation time (Figure 1). The rest of the i.r. spectrum
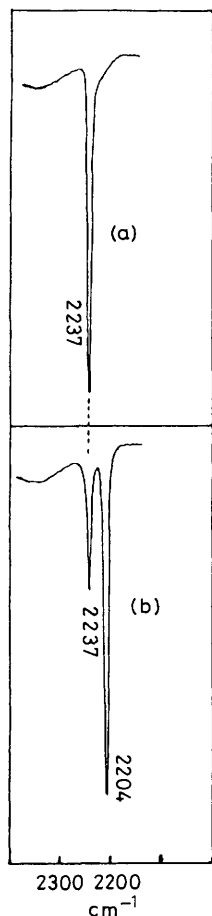
Figure 1. Infrared spectra (CN stretching region) of (1-py-β) (a) and the sample irradiated with a 400 W sun lamp for 4 h (b).

Figure 2. ¹H n.m.r spectrum of the reaction products isolated after irradiation (10 h) of (1-py-β) with sun light: (a) CH_3CH(CN)Co, (b) CH$_2$CH_2Co, (c) CH$_2$CH_2CN, (d) CH$_3$ of inplane ligand of (1-py-β), (e) CH$_3$ of inplane ligand of (1-py-α).

(1-py-β)	R = R′ = Me,	(1-py-α)
	X = CN, B = pyridine	
(1-PEA-β)	R = R′ = Me, X = CN,	(1-PEA-α)
	B = 1-phenylethylamine	
(1-ADPE-β)	R = R′ = Me, X = CN,	(1-ADPE-α)
	B = 2-amino-1,2-diphenylethanol	
(2-py-β)	R = Me, R′ = Ph,	(2-py-α)
	X = CN, B = pyridine	
(3-py-β)	R = R′ = Ph,	(3-py-α)
	X = CN, B = pyridine	
(4-py-β)	R = R′ = Me, X = CO$_2$Me,	(4-py-α)
	B = pyridine	

remained almost unchanged. T.l.c. of the crude extracts of the irradiated sample showed the presence of the dealkylated complex (R_f 0), the α-cyanoethyl complex (R_f 0.53), and starting material (R_f 0.59, solvent: acetone–benzene, 1:2), but no oxygen insertion product in spite of the aerobic conditions. The ¹H n.m.r. spectrum of the irradiated sample, after a column chromatographic isolation, showed new signals due to the α-cyanoethyl complex {δ 0.57 [d, CH_3CH(CN)Co], 2.24 and 2.26 [2 × s, HONC(CH_3)C(CH_3)NO]}[4] besides those of the starting material (Figure 2). The β-(methoxycarbonyl)ethyl group in bis(dimethylglyoximato)[β-(methoxycarbonyl)ethyl] (pyridine)cobalt(III) (4-py-β) was also proved to transform into the α-(methoxycarbonyl)ethyl group, as follows: new signals due to the α-(methoxycarbonyl)ethyl complex {δ 0.40 [d, CH_3CH(CO$_2$CH$_3$)Co], 2.2 (s, CH$_3$ of inplane ligand), and 3.49 (s, CO$_2$CH$_3$)}[4] appeared at the expense of signals due to starting material [δ 1.5—2.0 (m, CH$_2$CH$_2$CO$_2$), 2.14 (s, CH$_3$ of inplane ligand), and 3.58 (s, CO$_2$CH$_3$)].

In order to clarify the effects of structural variation on this isomerization, photoreactions of several β-cyanoethyl complexes (1-py-β), (1-PEA-β), (1-ADPE-β), (2-py-β), and (3-py-β) were examined by surveying the i.r. absorption intensity ratio of α-cyano and β-cyano groups of the sample irradiated under the standard conditions [a KBr disk (10 mm diameter) prepared from 99 mg of KBr powder and 1 mg of substrate was irradiated at 150 mm from a 400 W sun lamp]. The ratio of α-isomer to β-isomer of a sample was evaluated by
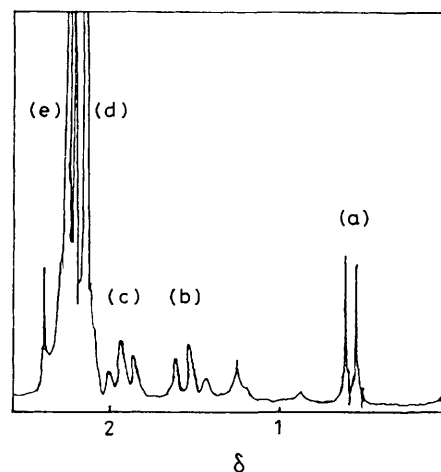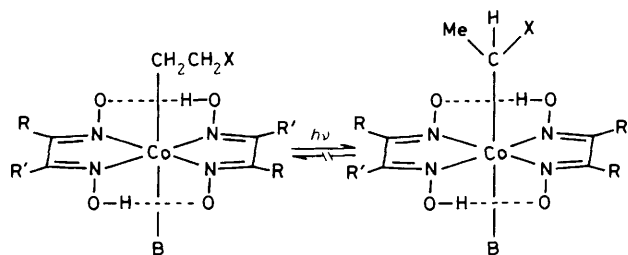
referring to the calibration curve of absorption intensity ratio of the α-cyano and β-cyano groups for the authentic α/β mixtures. In every β-cyanoethyl complex examined, the β-cyanoethyl group was transformed into a α-cyanoethyl group. The ratio α:β increased with irradiation time and the ratio approached a certain value asymptotically. In general, pyridine-co-ordinated complexes gave rather high values [(1-py-β) 1.5, (2-py-β) 1.5, (3-py-β) 9], but complexes co-ordinated with a base bearing strong sigma donor character afforded rather low values [(1-PEA-β) 0.2, (1-ADPE-β) 0.1] under the same conditions. The fact that the curve is asymptotic does not imply a reversible isomerization. In fact, no ν$_{CN}$ due to the β-cyanoethyl complex was detected in the spectrum of the irradiated KBr disk of α-cyanoethyl complexes (1-py-α), (1-PEA-α), (1-ADPE-α), (2-py-α), and (3-py-α). ¹H N.m.r. spectra of the irradiated samples,

(1-py-α) and (4-py-α), after a column chromatographic separation, were entirely in accord with those of the corresponding starting materials. These results clearly indicate that the reverse ($\alpha \rightarrow \beta$) isomerization does not occur. However, this does not imply that the Co–C bonds of α-substituted ethyl complexes are inert to light in the crystalline or solid state, since irradiation of the optically active (R)-(1-py-α) ([α]$_{578}$ +68.2°, $CHCl_3$)[5] and (R)-(4-py-α) ([α]$_{578}$ + 175°, $CHCl_3$)[5] afforded racemic (1-py-α) and (4-py-α), respectively.

For comparison with the solid state reaction, photoreactions were examined in benzene solution. But, neither ($\beta \rightarrow \alpha$) nor ($\alpha \rightarrow \beta$) isomerization was observed under Ar atmosphere, and under aerobic conditions, (1-py-α) and (1-py-β) gave the corresponding O_2 insertion products[6] without isomerization, i.e., α-cyanoethylperoxy and β-cyanoethylperoxy complexes, respectively.

The reasons why the solid state photoisomerization is completely unidirectional, and gives results quite different from those in solution are not clear at present.

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