Synthesis, Structure, and Solution Behaviour of the Compound *trans*-Bis(dimethylglyoximato)(ethyl)(methyl 4-pyridinecarboximidate)cobalt(III) †

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The synthesis of the title compound [Co(mpyim)(Hdmg)$_2$Et] (1), starting from [Co(4CN-py)(Hdmg)$_2$Cl] (mpyim = methyl 4-pyridinecarboximidate, 4CN-py = 4-cyanopyridine, and Hdmg = dimethylglyoximate monoanion) is reported. The compound crystallizes in the space group $P2_12_12_1$ with cell parameters a = 12.776(6), b = 9.606(5), c = 16.884(7) Å, and Z = 4. The structure was solved by Patterson and Fourier methods and refined by block-diagonal anisotropic least-squares methods to a final R value of 0.039 using 1 968 independent reflections having $I > 3\sigma(I)$ and using Mo-K_α radiation to a maximum 2θ = 56°. The N–Co–CH$_2$CH$_3$ fragment is characterized by N–Co–C and Co–C–C angles of 177.1(2) and 117.8(4)° respectively and by Co–N, Co–C, and C–C distances of 2.081(3), 2.035(5), and 1.519(8) Å respectively. Of the two possible configurations, E and Z, the imidate ester appears to prefer the E configuration in the solid state. ^{1}H N.m.r. lineshape analysis suggests that both the E and Z isomers are present in CDCl$_3$ solution, with relative populations (E:Z) of 4:1. These interconvert at a rate of 1.1×10^2 s^{-1} at 25 °C. Trace acid and base increase the rate of isomerization. The ligand exchange rate for the substitution of mpyim by P(OMe)$_3$ in CH$_2$Cl$_2$ shows that the reactivity of (1) is similar to that of the pyridine analogue.

Structural and conformational changes in coenzyme B$_{12}$ are believed to lead eventually to the Co–C bond homolysis step in many B$_{12}$ dependent enzymic reactions.[1] To understand the dependence of Co–C bond length and Co–C–R bond angle on systematic steric changes in organocobalt model compounds, we have investigated the effects of axial ligands with different electronic and steric properties on the structure,[1,2] reactions,[3,4] and spectral features [1,5] of Co–C containing cobaloximes. [The term cobaloxime refers to B$_{12}$ model compounds which contain the *trans*-bis(dioximate) arrangement. We have primarily investigated cobaloximes with the monoanion of dimethylglyoxime, Hdmg. Other abbreviations used are 4CN-py (4-cyanopyridine) and mpyim (methyl 4-pyridinecarboximidate).] We were particularly interested in characterizing the geometry of a C$_2$H$_5$ group bound to cobalt in this class of compounds since the structure of the only relevant ethyl complex, namely [Co(py)(Hdmg)$_2$Et],[6] was not determined accurately enough to be compared with other cobaloximes.[1] In addition, it was of some interest to determine the correct configuration of the MeOC(NH) residue in the solid state.

Experimental

Reagents.—Trimethyl phosphite (Aldrich) was distilled under vacuum before use. All other reagents were purchased from Aldrich and used without further purification.

Instrumentation.—Ligand exchange rates were monitored spectrophotometrically using a Durrum–Gibson D-110 stopped-flow spectrophotometer equipped with a thermostatted compartment (25.0 ± 0.04 °C).

Hydrogen-1 n.m.r. data were obtained on an IBM Instruments WP200SY spectrometer operating at 200.13 MHz, equipped with a Bruker B–VT.1000 variable-temperature unit which maintained the sample temperature to ±0.5 °C.

Ligand Exchange Rate Data.—Ligand exchange rates were monitored by stopped-flow methods as described previously.[4]

Hydrogen-1 *N.M.R. Spectra.*—High quality ^{1}H n.m.r. spectra were obtained from 0.18 mol dm^{-3} cobaloxime solutions in CDCl$_3$ subjected to four 90° pulses of 3.7 μs duration and accumulated as 16 000 data points in the time domain which transformed to 8 000 data points in the frequency domain. Data aquisition time was 3.4 s; relaxation delay time was 4.0 s.

Ligand Exchange Rate Analysis.—The experimental absorbance *versus* time rate data for the substitution of mpyim by P(OMe)$_3$ were treated with the standard integrated expression for a first-order process using linear least-squares analysis.

Under pseudo-first-order conditions {concentration of cobaloxime, [ML] = 0.02 mol dm^{-3}; P(OMe)$_3$, [L′] = 0.20 mol dm^{-3}}, where substitution proceeds by an S_N1 mechanism [1] (1), this analysis yields k_1 as the observed rate constant.

$$\begin{aligned} \mathrm{ML} &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M} + \mathrm{L} \\ \mathrm{M} + \mathrm{L'} &\xrightarrow{k_2} \mathrm{ML'} \end{aligned} \qquad (1)$$

Hydrogen-1 *N.M.R. Lineshape Analysis.*—Hydrogen-1 n.m.r. lineshapes were simulated using a published program [7] modified to be compatible with a UNIVAC UP-8180.

Observed spectral parameters used for lineshape fitting (P_A, P_B, T'_{2A}, T'_{2B}, Δv) were obtained from the stopped-exchange, low-temperature spectra (T = −57.0, −51.0,

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† *Supplementary data available* (No. SUP 23782, 11 pp.): H-atom co-ordinates, anisotropic thermal parameters, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

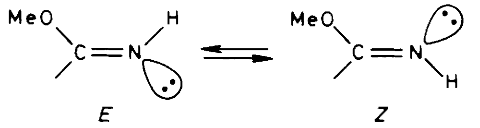

Figure 1. Configurational isomers of the imidate ester portion of [Co(mpyim)(Hdmg)$_2$Et]

−45.0, −39.0, and −32.0 °C) for the signals arising from the CH_3 groups of the imidate isomers (Figure 1).

Relative populations (P_A = 0.785, P_B = 0.215) and spin–relaxation rate constants (T'_{2A} = 0.094, T'_{2B} = 0.064 s; related to the peak half-height width, $W_{\frac{1}{2}} = 1/T'_2$) were independent of temperature in the stopped-exchange region.

The chemical shift difference between the two sites (Δν/Hz) varied linearly with temperature in the stopped-exchange region. Extrapolation to 25 °C gave Δν = 26.35 Hz.

The exchange constant τ ($\tau = P_B/k_f = P_A/k_r$), equation (2), was varied until the computer-simulated and experimental lineshapes were visually identical.

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B \qquad (2)$$

Preparation of [Co(mpyim)(Hdmg)$_2$Et] (1).—A mixture of [Co(4CN-py)(Hdmg)$_2$Cl] (3.0 g), C_2H_5I (1.5 cm^3), and NaOH (0.6 g) in methanol (300 cm^3) and a little water (5 cm^3) was stirred under N_2 for 5 min. $NaBH_4$ (0.3 g) in water (5 cm^3) was carefully added with immediate evolution of hydrogen. When the bubbling stopped, acetone (10 cm^3) was added and the solution reduced to 50 cm^3 on a rotary evaporator. The addition of water (100 cm^3) induced crystallization of the product (yield 73%) which was identified by ^{1}H n.m.r. ($CDCl_3$): δ 8.73 (m, 2 H, py), 7.57 (m, 2 H, py), 3.90 (m, 3 H, O–CH_3), 2.12 (s, 12 H, N=CCH_3), 1.72 (quartet, 2 H, Co–CH_2), 0.32 (t, 3 H, CH_2CH_3) [Found: C, 45.0; H, 6.0; N, 18.45 (Atlantic Microlab Inc.). Calc. for $C_{17}H_{27}CoN_6O_5$: C, 44.95; H, 6.0; N, 18.5%].

Crystals were obtained by dissolving the complex (0.3 g) in an acetone–water mixture (3 : 1, 40 cm^3) and allowing the acetone to evaporate in the dark at 5 °C.

Crystal Data.—$C_{17}H_{27}CoN_6O_5$, *M* = 454.4, Orthorhombic, space group $P2_12_12_1$, a = 12.776(6), b = 9.606(5), c = 16.884(7) Å, U = 2 072 Å^3, D_m = 1.47, Z = 4, D_c = 1.46 g cm^{-3}, $F(000)$ = 860, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 9.0 cm^{-1}; crystal dimensions 0.07 × 0.06 × 0.08 cm.

Cell parameters were determined from Weissenberg and Precession photographs and refined on a Siemens AED single-crystal diffractometer. One check reflection intensity, during the collection of diffraction data, was measured every 100 reflections and did not show any systematic variation throughout the data recording. A total of 2 874 ($2\theta_{max}$ = 56) data were collected and 1 968 of these, for which $I > 3\sigma(I)$, were corrected for Lorentz and polarization factors, but not for absorption, and used in the subsequent calculations.

Solution and Refinement of the Structure.—The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares methods. Hydrogen atoms, at calculated positions, and anisotropic temperature factors for non-hydrogen atoms were included in the final refinement. The contribution of the hydrogen atoms was held constant with B = 5 Å^2. The final R and R' values were 0.039 and 0.051 respectively. The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where A = 9.3 and B = 0.015 were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and sin(θ/λ). Atomic scattering factors were taken from ref. 8. All calculations were carried out using the computer programs from *X*-RAY 70.[9] Final positional parameters of non-hydrogen atoms are given in Table 1.

Table 1. Atomic positional parameters (× 10^4) of (1) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Co	1 565(0)	85(1)	289(0)
O(1)	1 420(3)	2 928(3)	773(2)
O(2)	2 589(3)	−1 035(4)	−1 075(2)
O(3)	1 766(3)	−2 755(3)	−176(2)
O(4)	356(3)	1 234(4)	1 553(2)
O(5)	5 919(3)	679(5)	2 780(2)
N(1)	1 818(3)	2 017(4)	226(2)
N(2)	2 366(3)	123(4)	−644(2)
N(3)	1 294(3)	−1 843(3)	333(2)
N(4)	659(3)	67(4)	1 169(2)
N(5)	2 896(3)	−127(4)	988(2)
N(6)	6 592(4)	−1 132(6)	2 093(3)
C(1)	2 620(5)	3 961(6)	−520(4)
C(2)	2 365(4)	2 455(5)	−363(3)
C(3)	2 697(4)	1 335(5)	−891(3)
C(4)	3 294(5)	1 533(7)	−1 649(4)
C(5)	426(5)	−3 776(5)	1 037(4)
C(6)	694(4)	−2 276(5)	887(3)
C(7)	265(4)	−1 132(5)	1 382(3)
C(8)	−541(4)	−1 332(7)	2 002(3)
C(9)	282(4)	198(5)	−422(3)
C(10)	−45(5)	1 624(6)	−723(4)
C(11)	3 038(4)	589(6)	1 661(3)
C(12)	3 982(4)	546(6)	2 086(3)
C(13)	4 796(4)	−261(5)	1 817(3)
C(14)	4 649(4)	−1 008(7)	1 137(3)
C(15)	3 692(4)	−923(6)	743(3)
C(16)	5 846(4)	−304(4)	2 227(3)
C(17)	6 915(5)	733(9)	3 204(4)

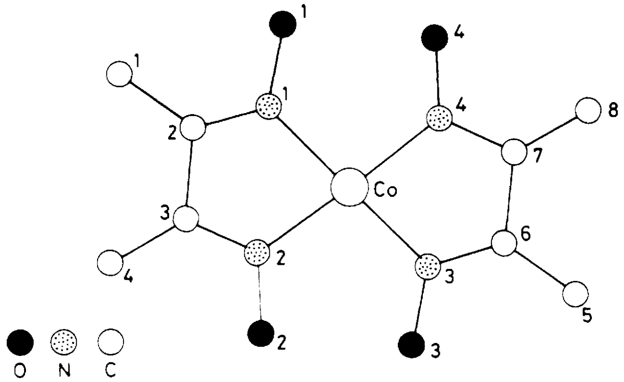

Figure 2. Numbering scheme for the atoms of the equatorial Co(Hdmg)$_2$ unit

Results and Discussion

Description and Discussion of the Structure.—The atom numbering scheme of the crystallographically independent molecule of (1) is given in Figures 2 and 3. Bond lengths and angles are listed in Table 2.

The four N atoms of the Co(Hdmg)$_2$ unit are coplanar within ±0.03 Å with the cobalt displaced 0.05 Å above their mean plane towards N(5). The two Hdmg units make an interplanar angle (α) of 9.1° with a flat helical distortion

Table 2. Bond lengths (Å) and relevant bond angles (°) of (1)

(*a*) Bond lengths

Co–N(5)	2.081(3)	N(2)–O(2)	1.360(5)	C(3)–C(4)	1.502(8)	C(12)–C(13)	1.374(7)
Co–C(9)	2.035(5)	N(2)–C(3)	1.307(6)	C(5)–C(6)	1.503(7)	C(13)–C(14)	1.368(7)
Co–N(1)	1.887(4)	N(3)–O(3)	1.367(5)	C(6)–C(7)	1.485(7)	C(14)–C(15)	1.394(8)
Co–N(2)	1.879(4)	N(3)–C(6)	1.280(6)	C(7)–C(8)	1.481(7)	C(13)–C(16)	1.511(7)
Co–N(3)	1.885(3)	N(4)–O(4)	1.352(5)	C(9)–C(10)	1.519(8)	C(16)–N(6)	1.261(7)
Co–N(4)	1.883(3)	N(4)–C(7)	1.307(6)	N(5)–C(11)	1.341(7)	C(16)–O(5)	1.333(7)
N(1)–O(1)	1.371(5)	C(1)–C(2)	1.506(7)	N(5)–C(15)	1.337(6)	O(5)–C(17)	1.460(8)
N(1)–C(2)	1.286(7)	C(2)–C(3)	1.460(7)	C(11)–C(12)	1.403(8)		

(*b*) Bond angles

C(9)–Co–N(5)	177.1(2)	N(3)–Co–N(4)	81.2(2)	N(5)–C(15)–C(14)	123.6(5)
N(1)–Co–N(2)	80.8(2)	N(3)–Co–N(5)	91.8(2)	C(11)–C(12)–C(13)	119.9(5)
N(1)–Co–N(3)	178.8(2)	N(3)–Co–C(9)	85.9(2)	C(12)–C(13)–C(14)	118.0(5)
N(1)–Co–N(4)	99.1(2)	N(4)–Co–N(5)	93.1(1)	C(12)–C(13)–C(16)	122.4(4)
N(1)–Co–N(5)	89.3(2)	N(4)–Co–C(9)	88.4(2)	C(13)–C(16)–N(6)	127.3(5)
N(1)–Co–C(9)	93.0(2)	Co–C(9)–C(10)	117.8(4)	C(13)–C(16)–O(5)	111.4(4)
N(2)–Co–N(3)	98.8(2)	Co–N(5)–C(11)	122.8(3)	C(13)–C(14)–C(15)	119.3(5)
N(2)–Co–N(4)	175.1(2)	Co–N(5)–C(15)	120.1(3)	C(14)–C(13)–C(16)	119.5(4)
N(2)–Co–N(5)	91.9(2)	C(11)–N(5)–C(15)	116.9(4)	N(6)–C(16)–O(5)	121.3(5)
N(2)–Co–C(9)	86.8(2)	N(5)–C(11)–C(12)	122.2(5)	C(16)–O(5)–C(17)	115.4(5)

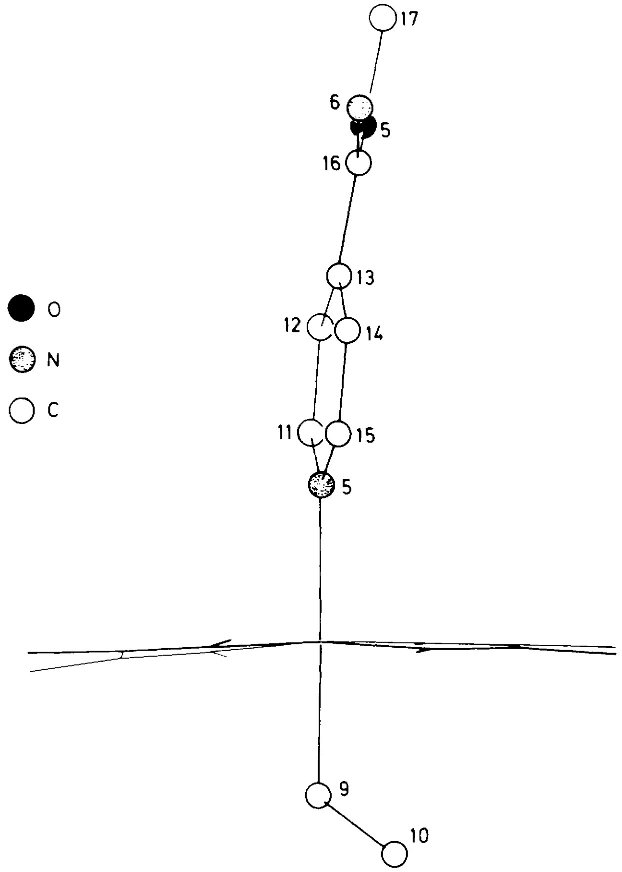

Figure 3. Side view of the molecule of (1) with the numbering scheme for the axial ligands

(Figure 3). This α value is larger than those reported [1] in other complexes of the type [Co(py)(Hdmg)$_2$X] (0.2—6.3°), consisting mainly of a bending towards one of the two axial ligands. However, the angle in (1) is the result of the bending towards the ethyl group and of the torsion, which produces the flat helical distortions, of the two Hdmg units Figure 3).

Bond lengths and angles of the equatorial moiety are quite normal.

The pyridine ring of the neutral ligand, planar within ±0.009 Å, is slightly rotated with respect to the ideal mirror plane which refers to the two Hdmg units. However it bends on the side of N(1) and N(2), making an angle of 96.7° with the plane passing through the four equatorial N atoms.

The N(5)–Co–C(9)–C(10) fragment is characterized by N–Co–C and Co–C–C angles of 177.1(2) and 117.8(4)° respectively. The Co–N, Co–C, and C–C bond lengths are 2.081(3), 2.035(5), and 1.519(8) Å respectively. These values should be compared with those reported for [Co(py)(Hdmg)$_2$Et]:[6] Co–C–C [122.4(8)°], Co–N [2.084(7) Å], Co–C [2.07(1) Å], and C–C [1.49(2) Å], although the latter values are of lower accuracy.

The Co–N and Co–C distances and the Co–CH$_2$–R angle fit into the trends reported for a series of [Co(py)(Hdmg)$_2$(CH$_2$R)] compounds [1] (R = SiMe$_3$, CMe$_3$, H, CO$_2$Me, or NO$_2$). In fact in the above series the Co–C distance and the Co–CH$_2$–R angle increased with the increasing bulk of R in a range from 1.998(6) (R = H) [10] to 2.060(6) Å (R = CMe$_3$) [1] and from 113.7(2) (R = NO$_2$) [11] to 130.3(4)° (R = CMe$_3$) [1] respectively. On the other hand, the Co–N distance increased with the increasing electron-donor power of R in a range going from 2.028(3) (R = NO$_2$) [11] to 2.091(5) Å (R = SiMe$_3$).[1] In (1) the Co–C bond length is very close to the value of 2.040(6) Å reported for R = CO$_2$Me,[12] whereas the Co–N bond length is the same as that reported for R = CMe$_3$.[1] The above comparison and ligand exchange rate results indicate that the MeOC(NH) group bound to pyridine has little, if any, influence on the structure and reactivity of (1) with respect to the pyridine analogue.

As usually found [13] in cobaloximes having σ-bonded CH$_2$R groups, the orientation of the ethyl group in (1) is such that the CH$_2$–CH$_3$ bond lies almost on one of the Co–N(eq.) equatorial bonds, namely Co–N(1). Such an orientation provokes an opening of the N(1)–Co–C(9) angle, which is 93.0(2)°, whereas the other N(eq.)–Co–C(9) angles range from 85.9(2) to 88.4(2)°. Structural parameters of the pyridine ring substituent agree well with the expected imidate ester geometry. The C(16), C(17), O(5), and N(6) atoms are coplanar within ±0.003 Å and their plane makes an angle of 11.7° with that of the pyridine ring. The C(16)–N(6) bond length of

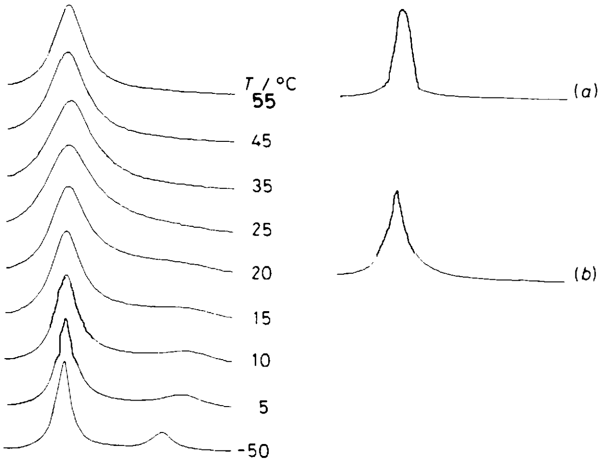

Figure 4. Hydrogen-1 n.m.r. spectra of [Co(mpyim)(Hdmg)$_2$Et] (0.052 mol dm^{-3}) in CDCl$_3$ showing only the bands arising from the CH$_3$ group of the imidate ester: (*a*) 25.0 °C, with 0.5 µl of glacial acetic acid added; (*b*) 25.0 °C, with 1.0 µl of 2,6-dimethylpyridine added

1.261(7) Å suggests a C=N double bond, as that of 1.260(4) Å reported for MeC(O)CH=NOH.[14] The C(16)–O(5) distance of 1.333(7) Å is very close to those reported for the C–OH bond found in carboxylic acids or that of 1.358 Å reported for the CH$_2$=CH–OMe bond.[15] Finally, the C(13)–C(16) distance of 1.511(7) Å suggests that this bond is mainly a single bond.

Configuration of the mpyim ligand. The location on the Fourier-difference map of the hydrogen atom attached to N(6) and the geometry around C(16) atom suggest that the configuration *E* of Figure 1 is preferred in the solid state. In fact the angle C(13)–C(16)–N(6) of 127.3(5)°, compared with the angle C(13)–C(16)–O(5) of 111.4(4)°, may be a consequence of the relief of the steric strain between the hydrogen atoms attached to C(14) and N(6) [note that the *Z* configuration would probably be even more sterically strained due to interactions between the hydrogen on C(14) and the bulkier lone pair of electrons on N(6)]. In general, imidates have been shown to prefer the *E* configuration.[16] Factors which determine the *E* : *Z* ratio are dipolar interactions and steric effects;[17] *E* : *Z* ratios for imidates are typically in the range 0—50 : 1.[16-19]

No short (<3.2 Å) intermolecular distance involving N(6) was detected, thus hydrogen bonding does not influence the geometry of the imidate in the solid state. It is therefore likely that the *E* configuration predominantly exists in CDCl$_3$ solution as well, since the solvent is incapable of hydrogen bonding.

Hydrogen-1 n.m.r. data indicate that one of the imidate isomers is preferred over the other by 4 : 1 in CDCl$_3$. Based on the structural data, the predominant isomer in CDCl$_3$ is probably also of the *E* configuration.

Ligand Exchange Rate.—The reactivity of mpyim (k_1 = 2.5 × 10^{-1} s^{-1}) is less than 4CN-py (k_1 = 9.6 × 10^{-1} s^{-1})[20] by a factor of 3.8 for ethylcobaloximes; *i.e.* its reactivity is similar to pyridine.

Discussion of the E–Z *Isomerization.*—Mechanisms which have been proposed for *E* to *Z* isomerization of imidates include: (*a*) base-catalyzed enamine isomerization (impossible for mpyim);[18] (*b*) reversible nucleophilic addition of some nucleophile to the double bond of the protonated imidate;[18] (*c*) uncatalyzed rotation about the C–N bond;[18] (*d*) inversion of the lone pair on nitrogen;[18] and (*e*) proton transfer.[16] The inversion mechanism has been well established as the predominant pathway for *E–Z* isomerization about free carbon–nitrogen double bonds.[21,22] For example, rate constants reported for lone-pair inversion in some N-substituted imines range from $k = 3.6 \times 10^1$ to 6.6×10^3 s^{-1}.[22] Isomerization of (1) proceeds at the rate $1/\tau = 1.1 \times 10^2$ s^{-1}, at 25 °C. It is therefore possible that the *E–Z* isomerization of (1) proceeds *via* the lone-pair inversion mechanism in the absence of acid or base, based on the observed rate at 25 °C.

Trace acid and base increased the rate of isomerization to the fast-exchange limit (Figure 4). Thus ^{1}H n.m.r. spectra of impure samples show only one O–CH$_3$ peak and may be mistaken to be isomerically pure.

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