Study of Reactions Between Alkyl(pyridine)cobaloximes and Trifluoroacetic Acid; Formation and Crystal Structure of *cis*-Bis(butane-2,3-dione dioxime)bis(trifluoroacetoxy)cobalt(II)

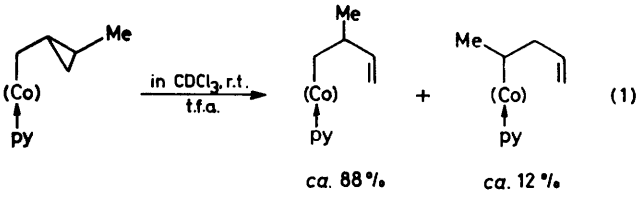
By **Nathaniel W. Alcock, Martin P. Atkins, Bernard T. Golding,*** and **Philip J. Sellars,** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

The reactions between several alkyl(pyridine)cobaloximes [$CoR(Hdmg)_2(py)$] [R = Me, CH_2Cl, $CHCl_2$, Et, Pr^i, Bu^n, $CH_2CH_2CH{=}CH_2$, or $CH_2CHMeCH{=}CH_2$, (1a)—(1h) respectively; py = pyridine; Hdmg = monoanion of dimethylglyoxime] and trifluoroacetic acid in deuteriochloroform have been monitored by ^1H n.m.r. spectroscopy. This technique indicates that addition of trifluoroacetic acid to an alkyl(pyridine)cobaloxime initially causes reversible protonation without loss of pyridine, then a second protonation occurs leading to the loss of pyridine as pyridinium trifluoroacetate. With excess of trifluoroacetic acid, the alkylcobaloximes lose their alkyl group as RH [*e.g.* propane from (1e)] and slowly deposit a red crystalline solid, identified as the title complex (4) by analysis of its crystal structure. Crystals of (4) are triclinic, space group $P\bar{1}$, with a = 10.068(3), b = 10.716(5), c = 13.030(3) Å, α = 100.15(3), β = 116.76(3), γ = 88.97(3)°, and Z = 2. 1 873 Reflections collected at −80 °C by a four-circle diffractometer were refined to R = 0.053. The Co–O distances are 2.069(2) and 2.057(2) Å and Co–N are 2.126(3), 2.138(2), 2.139(3), and 2.149(3) Å.

REACTIONS between acids and alkylcobaloximes take various courses depending upon the type of alkyl group and the axial base of the cobaloxime [*e.g.* pyridine (py), water, triphenylphosphine]. If the alkyl group is labile to acid, *e.g.* as in [$CoR(Hdmg)_2(py)$] {R = 3-(4′-methyl-2′,6′,7′-trioxabicyclo[2.2.2]octyl)propyl, Hdmg = dimethylglyoximate(1—)}, reaction takes place entirely at the alkyl group leaving the remaining functionalities of the cobaloxime intact. Thus, the above complex undergoes ready hydrolysis in 0.05 mol dm^{-3} hydrochloric acid to yield [7,7-di(hydroxymethyl)-4-oxo-5-oxa-octyl]bis(dimethylglyoximato)(pyridine)-cobalt in almost quantitative yield.[1]

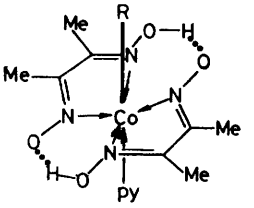
For alkyl(pyridine)cobaloximes, liganded pyridine may participate as a Brønsted base in equilibrium with aqueous oxonium ion. Thus, some alkyl(pyridine)-cobaloximes may be converted into alkyl(aquo)cobaloximes when treated with aqueous acid,[2] and such reactions have been used for preparative purposes.[2,3]

The interconversions of substituted cyclopropylmethyl- and but-3-enyl(pyridine)-cobaloximes in chloroform solution [*e.g.* equation (1), r.t. = room temperature] are catalysed by trifluoroacetic acid (tfa).[4-6] A likely role for the trifluoroacetic acid is to remove co-ordinated pyridine (py) from the cobaloxime, generating a formally five-co-ordinate de-pyridinecobaloxime. It is such intermediates which are considered to be possible precursors of the homoallyl–cobalt intermediates or transition states proposed for the interconversions of but-3-enyl- and cyclopropylmethyl-cobaloximes.[5,6]



(1)

We now report a study of the reactions of trifluoroacetic acid with several alkyl(pyridine)cobaloximes, (1a)—(1h), under non-aqueous conditions. We have sought to probe the possible competition between



(1a; R = Me) (1e; R = Pr^i)
(1b; R = CH_2Cl) (1f; R = Bu^t)
(1c; R = $CHCl_2$) (1g; R = $CH_2CH_2CH{=}CH_2$)
(1d; R = Et) (1h; R = $CH_2CHMeCH{=}CH_2$)

protonation of the bis(dimethylglyoximato)-system of an alkyl(pyridine)cobaloxime and removal of its pyridine (as protonated pyridine). The cobalt-containing product of these reactions has been shown by X-ray crystallography to be a *cis*-cobaloxime(II) species.[7]

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded at 220 MHz using a Perkin-Elmer R34 instrument. The spectrometer probe was thermostatted at 298 ± 0.5 K. Single-crystal X-ray diffraction measurements were made with a Syntex $P2_1$ four-circle diffractometer. Bulk paramagnetic susceptibilities were measured by the Gouy technique at ambient temperature (297 K) and were corrected for diamagnetic contributions by means of Pascal's constants. Microanalytical determinations of C, H, and N were carried out by C. H. N. Analysis Ltd., Leicester. Gas–liquid chromatograms were recorded on a Perkin-Elmer F11 instrument (N_2 carrier, flame ionisation detection). Infrared spectra were recorded on a Perkin-Elmer 257 instrument.

Trifluoroacetic acid, tfa (Fisons), was purified before use by distillation from phosphorus(v) oxide. Alkyl(pyridine)-cobaloximes were prepared by standard procedures.[8] A

solution of trifluoroacetic acid in deuteriochloroform was prepared from the acid (1 cm^3) by diluting to 5 cm^3. The concentration (*ca.* 5.2 mol dm^{-3}) of trifluoroacetic acid in this solution was determined by titration with standard aqueous sodium hydroxide using ethanol as co-solvent and with phenolphthalein as indicator. Samples for n.m.r. measurements were prepared by dissolving the cobaloxime (30, 45, or 60 mg) in deuteriochloroform, adding a known volume of the standardised trifluoroacetic acid solution, and diluting with deuteriochloroform to a total volume of 0.600 cm^3 in an n.m.r. tube. All solutions were dispensed using an all-glass ' Agla ' micrometer syringe. A series of samples for each fixed total cobalt concentration, but with $0 <$[total tfa]/[total Co] < 10, was prepared, and the ^1H n.m.r. spectra recorded within 1 h of mixing. It was found that using deoxygenated solvent had no observable effect on either the spectra obtained or the results calculated therefrom.

Crystalline samples of bis(butane-2,3-dione dioxime)-bis(trifluoroacetoxy)cobalt(II) were obtained by allowing the solutions of greatest [total tfa]/[total Co] to stand either in diffuse daylight or in the dark at room temperature for 1—2 d. The deep red crystals were then filtered off on a glass sinter and washed first with a little cold solvent and then with hexane. The crystals were air-dried and final traces of solvent were removed by pumping at 10—12 mmHg * pressure for a few hours. Samples of the cobaloxime(II) obtained from (1e) and (1g) gave identical diffraction patterns. A larger sample of bis(butane-2,3-dione dioxime)bis(trifluoroacetoxy)cobalt(II) was obtained by dissolving isopropyl(pyridine)cobaloxime (1e) in dichloromethane (15 cm^3) at room temperature and adding trifluoroacetic acid (2 cm^3). The flask, containing a clear dark solution, was stoppered with a rubber septum and allowed to stand for 2 d. The crystals were filtered from the clear solution, washed with a little dichloromethane and then with hexane, before drying in air and finally at reduced pressure (Found: C, 27.8; H, 3.00; N, 11.0. Calc. for $C_{12}H_{16}CoF_6N_4O_8$: C, 27.85; H, 3.10; N, 10.8%). A microcrystalline sample had a bulk molar magnetic susceptibility of $8\,350 \times 10^{-6}$ c.g.s. units at 297 K, corresponding to an effective magnetic moment of 4.45 μ_B.

Propane, produced by reaction of (1e) with tfa, was identified by gas–liquid chromatography (g.l.c.) at room temperature using a column (6 ft × 1/16 in) packed with n-octane on Porasil C (100—120 mesh). Gas samples withdrawn from the vapour above the mixture of (1e) and tfa showed a single peak, which co-chromatographed with an authentic sample of propane on the g.l.c. trace.

Crystal Data.—$C_{12}H_{16}CoF_6N_4O_8 \cdot CHCl_3$, at −80 °C M = 636.6, Triclinic, $P\bar{1}$, a = 10.068(3), b = 10.716(5), c = 13.030(3) Å, α = 100.15(3), β = 116.76(3), γ = 88.97(3)°, U = 1 232.6(8) Å^3, Z = 2, D_c = 1.543 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 9.88 cm^{-1}.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 45°, with scan range ±0.75° (2θ) around the $K_{\alpha1}$—$K_{\alpha2}$ angles, scan speed 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. To avoid decomposition, the temperature was held at −80 °C with the LT-1 controller.

Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 14 high-angle reflections. 1 873 Observed reflections [$I/\sigma(I) > 3.0$] were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR; [9] maximum and minimum transmission factors were 0.95 and 0.77.

Structure Solution and Refinement.—Space group $P\bar{1}$ was assumed and shown to be correct by successful refinement. The Co was located from a Patterson synthesis, and light atoms found from Fourier syntheses. Refinement was slow until the $CHCl_3$ solvent was located and until the fluorine atoms were refined anisotropically. It was found that one CF_3 group was disordered and its fluorine atoms were placed in two sets of positions at 50% occupancy; the other CF_3 is ordered. After anisotropic refinement, all hydrogen atoms could be seen on a difference-Fourier

TABLE 1

Atomic co-ordinates (× 10^4) with standard deviations in parentheses

Atom	x	y	z
Co	4 581.7(4)	598.0(4)	2 448.7(3)
O(1)	2 875(3)	−979(2)	3 381(2)
O(2)	2 551(3)	2 229(2)	606(2)
O(3)	4 000(3)	2 949(2)	3 990(2)
O(4)	7 060(2)	1 138(2)	1 696(2)
O(5)	6 427(2)	−194(2)	3 589(2)
O(6)	5 703(3)	−1 431(2)	4 485(2)
O(7)	4 208(2)	−1 068(2)	1 269(2)
O(8)	5 969(2)	−1 210(2)	651(2)
N(1)	2 829(3)	−58(2)	2 748(2)
N(2)	2 593(3)	1 312(2)	1 254(2)
N(3)	4 936(3)	2 448(2)	3 524(2)
N(4)	6 162(3)	1 638(2)	2 190(2)
C(1)	139(6)	−244(6)	2 125(6)
C(2)	1 510(5)	277(4)	2 141(4)
C(3)	1 446(5)	1 212(5)	1 419(4)
C(4)	83(6)	1 961(6)	906(6)
C(5)	5 525(7)	4 693(4)	3 603(5)
C(6)	5 637(5)	3 292(4)	3 331(4)
C(7)	6 575(5)	2 761(4)	2 778(4)
C(8)	7 924(6)	3 521(5)	2 963(5)
C(9)	6 579(5)	−1 026(4)	4 169(4)
C(10)	8 049(6)	−1 686(5)	4 510(5)
C(13)	9 101(8)	3 739(7)	7 549(7)
C(11)	4 972(5)	−1 634(4)	832(4)
C(12)	4 627(6)	−3 083(5)	491(5)
Cl(1)	11 030(2)	3 867(2)	8 369(2)
Cl(2)	8 586(4)	4 613(4)	6 446(3)
Cl(3)	8 299(4)	4 246(6)	8 437(4)
F(101)	7 897(12)	−2 629(15)	3 712(10)
F(102)	8 385(13)	−2 187(18)	5 470(12)
F(103)	9 147(10)	−967(14)	4 757(21)
F(104)	8 633(28)	−1 649(31)	3 806(21)
F(105)	9 092(19)	−1 123(30)	5 473(18)
F(106)	7 944(21)	−2 843(18)	4 529(43)
F(121)	5 249(6)	−3 593(3)	1 442(3)
F(122)	3 184(4)	−3 407(3)	−23(4)
F(123)	5 156(5)	−3 630(3)	−226(4)
H(1)	3 885(75)	−1 122(63)	3 794(58)
H(2)	3 252(86)	2 003(74)	306(68)
H(3)	4 019(102)	2 376(86)	4 432(80)
H(4)	6 704(90)	274(76)	1 361(70)
H(11)	−390(76)	418(66)	2 267(60)
H(12)	198(92)	−590(79)	2 799(75)
H(13)	−416(107)	−739(92)	1 466(87)
H(41)	−213(121)	2 376(103)	1 476(99)
H(43)	−812(103)	1 383(91)	325(81)
H(51)	5 992(116)	5 106(94)	3 323(89)
H(52)	5 351(119)	4 919(94)	4 253(100)
H(53)	4 477(111)	4 901(85)	3 254(89)
H(81)	7 780(122)	3 717(104)	2 279(97)
H(82)	8 310(100)	4 134(86)	3 641(80)
H(83)	8 618(109)	3 031(93)	2 970(86)
H(42)	79(134)	2 618(117)	398(107)

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

synthesis except for that of the $CHCl_3$; they were refined with isotropic thermal parameters. Final refinement by least squares (in large blocks) gave $R = 0.053$. Weights were used of the form $W = A \times B$, where $A = 1.0$ or $30.0/F$, if $F > 30.0$, $B = 1.0$ or $[(\sin\theta)/\lambda]/0.4$ if $[(\sin\theta)/\lambda] < 0.4$. The only residual peaks on a difference-Fourier synthesis, of height <0.5—1.1 e Å^{-3}, were in the vicinity of the $CHCl_3$, no doubt due to slight errors in the

TABLE 2

Selected bond lengths (Å) and angles (°) with standard deviations in parentheses *

Co–O(5)	2.069(2)	O(5)–Co–O(7)	86.60(9)
Co–O(7)	2.057(2)	O(5)–Co–N(1)	103.14(11)
Co–N(1)	2.126(3)	O(5)–Co–N(3)	97.71(9)
Co–N(2)	2.139(3)	O(5)–Co–N(4)	84.86(10)
Co–N(3)	2.149(3)	O(7)–Co–N(1)	87.92(11)
Co–N(4)	2.138(2)	O(7)–Co–N(2)	91.21(9)
		O(7)–Co–N(4)	101.68(11)
		N(1)–Co–N(2)	73.95(11)
		N(1)–Co–N(3)	95.73(11)
		N(2)–Co–N(3)	84.72(9)
		N(2)–Co–N(4)	98.34(11)
		N(3)–Co–N(4)	74.05(11)
O(5)–C(9)	1.231(6)	C(9)–O(5)–Co	133.2(3)
C(9)–C(10)	1.539(8)	O(5)–C(9)–C(10)	114.9(5)
C(9)–O(6)	1.241(7)	O(5)–C(9)–O(6)	129.4(4)
C(10)–F	1.280(19)av.	O(6)–C(9)–C(10)	115.7(5)
O(7)–C(11)	1.242(6)	C(11)–O(7)–Co	133.0(2)
C(11)–C(12)	1.538(6)	O(7)–C(11)–C(12)	113.8(5)
C(11)–O(8)	1.239(7)	O(7)–C(11)–O(8)	129.8(4)
C(12)–F	1.322(7)av.	O(8)–C(11)–C(12)	116.4(5)
N(1)–O(1)	1.380(4)	Co–N(1)–O(1)	127.3(2)
N(1)–C(2)	1.287(5)	Co–N(1)–C(2)	117.6(3)
C(2)–C(1)	1.489(9)	O(1)–N(1)–C(2)	114.1(4)
C(2)–C(3)	1.473(8)	N(1)–C(2)–C(3)	114.3(5)
C(3)–C(4)	1.515(8)	C(1)–C(2)–N(1)	124.1(5)
C(3)–N(2)	1.276(7)	C(1)–C(2)–C(3)	121.6(4)
N(2)–O(2)	1.392(4)	C(2)–C(3)–N(2)	115.0(5)
C(1)–H	0.93(9)av	C(2)–C(3)–C(4)	120.9(6)
C(4)–H	1.00(12)av.	N(2)–C(3)–C(4)	124.1(5)
		Co–N(2)–O(2)	125.6(2)
		Co–N(2)–C(3)	116.3(3)
		C(3)–N(2)–O(2)	114.8(3)
N(3)–O(3)	1.389(4)	Co–N(3)–O(3)	124.7(2)
N(3)–C(6)	1.281(6)	Co–N(3)–C(6)	115.4(3)
C(6)–C(5)	1.495(6)	O(3)–N(3)–C(6)	113.7(3)
C(6)–C(7)	1.478(8)	N(3)–C(6)–C(7)	113.9(4)
C(7)–C(8)	1.497(9)	N(3)–C(6)–C(5)	124.7(5)
C(7)–N(4)	1.271(5)	C(5)–C(6)–C(7)	121.4(5)
C(5)–H	0.93(12)av.	C(6)–C(7)–N(4)	114.8(4)
C(8)–H	0.90(10)av.	C(6)–C(7)–C(8)	120.1(4)
		N(4)–C(7)–C(8)	125.0(5)
O(1)–H(1)	0.94(7)	N(1)–O(1)–H(1)	106(5)
O(2)–H(2)	0.96(10)	N(2)–O(2)–H(2)	106(5)
O(3)–H(3)	0.91(11)	N(3)–O(3)–H(3)	102(7)
O(4)–H(4)	0.95(8)	N(4)–O(4)–H(4)	106(6)
O(6)–H(1)	1.69(7)	C(9)–O(6)–H(1)	118(3)
O(6) · · · O(1)	2.63(3)		
O(6)–H(3^{I})	1.80(11)	C(9)–O(6)–H(3)	131(3)
O(6) · · · O(3^{I})	2.696(4)		
O(8)–H(4)	1.69(7)	C(11)–O(9)–H(4)	117(4)
O(8) · · · O(4)	2.634(3)		
O(8)–H(2^{II})	1.84(10)	C(11)–O(9)–H(2)	128(2)
O(8) · · · O(2^{II})	2.758(4)		

* Roman numeral superscripts denote the transformations: I $1-x, -y, 1-z$; II $1-x, -y, -z$.

correction for thermal motion. Final atomic co-ordinates are in Table 1 and bond lengths and angles are in Table 2. Thermal parameters and final structure factors are listed in Supplementary Publication No. SUP 23177 (27 pp.).* All computing was with the '*X*-RAY '76' system [10] on a Burroughs B6700 computer.

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

RESULTS AND DISCUSSION

Studies by N.M.R. Spectroscopy of the Reactions between tfa and Alkylcobaloximes.—For all the alkyl(pyridine)-cobaloximes used, changes in the ^1H n.m.r. spectra, consequent upon the addition of increasing aliquots of trifluoroacetic acid (tfa), exhibit a general trend. Hydrogen-1 n.m.r. spectra obtained from the reactions of but-3-enyl(pyridine)cobaloxime with tfa are shown in Figure 1(*a*)—(*d*). For fixed total cobalt concentration

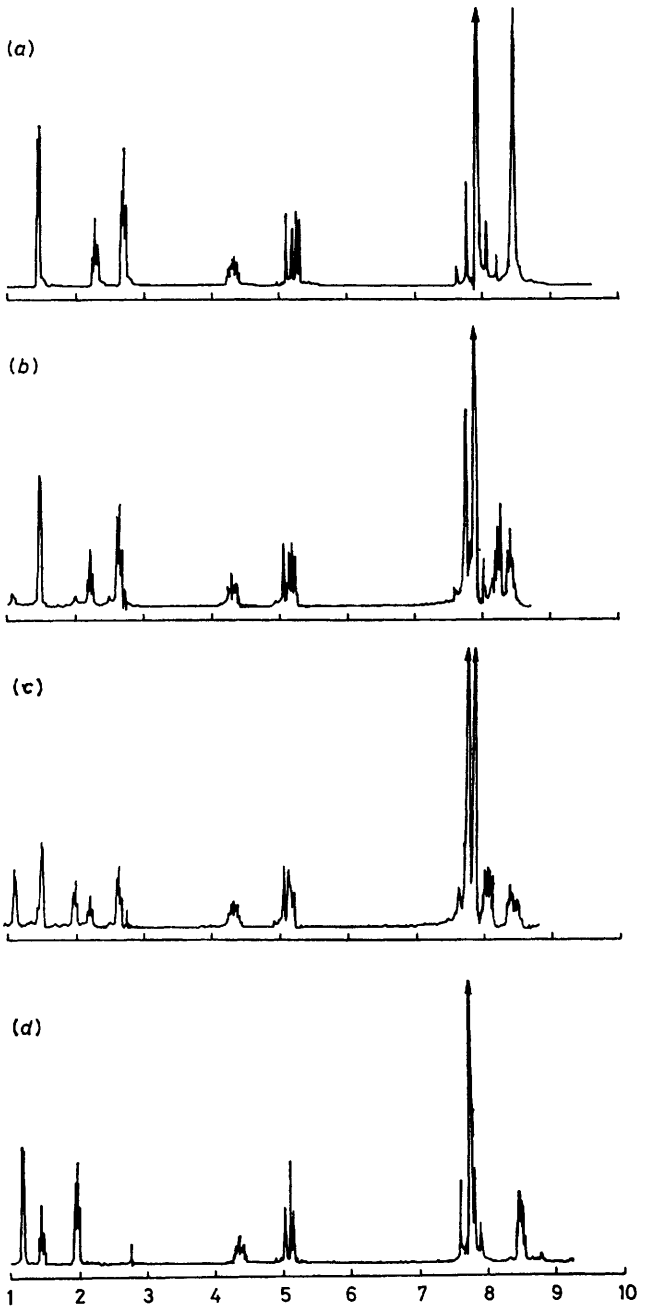


FIGURE 1 Proton n.m.r. spectra of but-3-enyl(pyridine)cobaloxime in $CDCl_3$ containing the following mol equivalents of trifluoroacetic acid: (*a*) 0, (*b*) 1.5, (*c*) 2.5, (*d*) >10

and $0 <$ [tfa]/[total cobalt] < 10, new resonances appear at δ 8.05, 8.55, and 8.80 (due to pyridinium trifluoroacetate). These resonances are unambiguously assigned by comparison with a spectrum of authentic pyridinium trifluoroacetate and by their increase in intensity on addition of this salt. As the relative concentration of tfa is increased, the resonances at δ 8.05, 8.55, and 8.80 increase in intensity, whilst those at δ 7.30, 7.72, and 8.55 (originally present in the neutral cobaloxime) decrease in intensity. The total integrated intensity of all the pyridine-derived resonances is constant throughout the incremental additions of tfa. For [tfa]/[total cobalt] > 11, no detectable pyridine resonances from alkyl(pyridine)cobaloxime were observed. Whence, all the pyridine originally present in the alkyl(pyridine)-cobaloxime is in the form of pyridinium trifluoroacetate.

But-3-enyl(pyridine)cobaloxime has a sharp resonance at δ 2.12 from the magnetically and chemically equivalent methyl groups of the dimethylglyoximato-ligands. Addition of tfa causes a new singlet resonance at δ 2.30 to appear. As the relative concentration of tfa is increased, this resonance also increases in intensity with concomitant loss of intensity of the resonance at δ 2.12. For [tfa]/[total cobalt] > 11, the resonance at δ 2.12 is not detectable; only a single resonance at δ 2.30 (12 H) is observed. The gradual increase in intensity of the resonance at δ 2.30 qualitatively parallels the increase in intensities of the resonances from pyridinium trifluoroacetate. No quantitative comparison was possible because of the unreliability of the integrals in the region δ 2.1—2.3 caused by overlapping of the intense dimethylglyoximato-resonances.

Changes in the resonances of the protons of the alkyl side chain are rather more complicated to analyse. There are variations both in the positions of these resonances and their multiplicity. For $R = CH_2CH_2$-$CH{=}CH_2$ the resonance at δ 1.55 in the neutral cobaloxime due to the $2 \times CH_2$ protons (*i.e.* two overlapping multiplets) gradually divides into two distinct multiplets at δ 1.6 and 1.8 [*cf.* Figure 1(*b*)] upon incremental addition of tfa. The olefinic CH_2 resonance, centred at δ 4.86, changes from a four-component multiplet in the neutral cobaloxime to a three-component multiplet on addition of tfa. Only very minor changes in the multiplicity of the olefinic C*H* resonance were observed. On further addition of tfa [*cf.* Figure 1(*c*)] the multiplet at δ 1.6 [Figure 1(*b*)] splits into two multiplets (δ 1.5 and 1.62), whilst the multiplet at δ 1.8 [Figure 1(*b*)] changes its appearance and moves to lower field (*ca.* δ 1.9). With more tfa the multiplet at δ 1.5 grows in intensity [*cf.* Figure 1(*d*)], whilst that at δ 1.62 gradually disappears. The multiplet at δ 1.9 [Figure 1(*c*)] shifts under the resonance from dimethylglyoxime methyls [δ 2.3, Figure 1(*d*)].

To investigate more fully the identity of the resonances, a series of off-resonance decoupling experiments were performed on solutions of but-3-enyl-(pyridine)cobaloxime. Irradiation of the multiplet at δ 1.55 caused the olefinic resonances at δ 4.8 and 5.7 to collapse to the classical ABX pattern of 12 lines (*cf.* Figure 2). Here $|J_{AB}| = 2.2$ Hz and $|J_{AB} + J_{BX}| = 26.9$ Hz with $|J_{AX}| = 9.9$ Hz and $|J_{BX}| = 17.1$ Hz. For a solution of but-3-enyl(pyridine)cobaloxime containing tfa in which [tfa]/[total cobalt] = 8, assignment of the resonances from the CH_2 groups is possible. Thus, the multiplet centred at δ 1.52 collapses to a triplet ($J = 8.5$ Hz) when the olefinic methine proton is irradiated but is

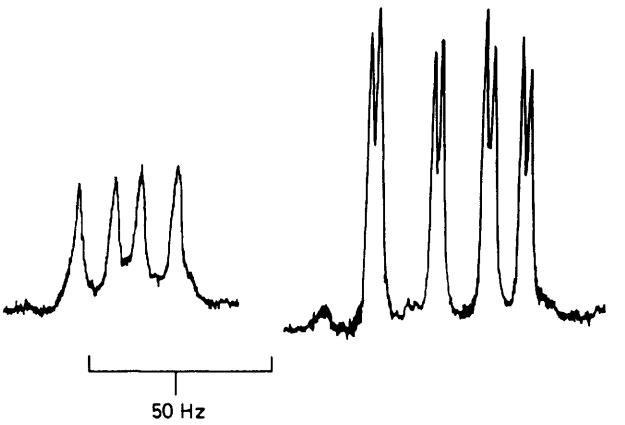


FIGURE 2 Proton n.m.r. resonances from the olefinic protons of but-3-enyl(pyridine)cobaloxime in $CDCl_3$ (after simultaneous irradiation of the adjacent methylene group)

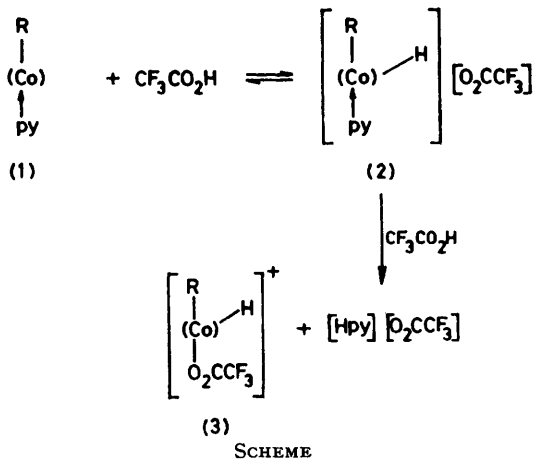
essentially unaltered (*i.e.* remaining as an apparent quartet) on irradiation of the olefinic methylene protons. This shows that the resonance at δ 1.52 arises from the methylene group β to cobalt. Irradiation of the olefinic methine proton causes no change in multiplicity of the resonance centred at δ 2.16. This multiplet is assigned to the methylene group directly bonded to cobalt.

Irradiation of the signal at δ 1.52 causes the resonance from the olefinic methine proton to collapse to a four-component multiplet (*i.e.* the X resonance of an ABX system) with $|J_{AX}|$ *ca.* 9.8 Hz and $|J_{BX}|$ *ca.* 17.1 Hz. These values are similar to those found for the neutral but-3-enyl(pyridine)cobaloxime and correspond to *Z* olefinic coupling (J_{AX}) and *E* olefinic coupling (J_{BX}).

The observation that addition of tfa to an alkyl-(pyridine)cobaloxime causes shifts of the resonances of the cobaloxime as well as the appearance of new resonances can be rationalised in terms of stepwise equilibria involving the cobaloxime and acid.* A minimum of two such processes is indicated. At least one, rapid on the ^1H n.m.r. time scale, is associated with shifts in resonances and at least one other, slow on the ^1H n.m.r. time scale, accounts for the appearance of new peaks.

To account for the shifts observed in the positions of resonances of the alkyl and pyridine groups in the ^1H n.m.r. spectrum, an empirical model was set up, illustrated in the Scheme. Two equilibria are recognised. The first is a reversible monoprotonation of the alkyl-(pyridine)cobaloxime and it is this equilibrium which is considered to be rapid on the ^1H n.m.r. time scale. It

* Dr. M. D. Johnson (University College) independently made this observation with tfa and ethyl(pyridine)cobaloxime (personal communication).



SCHEME

has already been demonstrated that such equilibria do occur for solutions of alkylcobaloximes and aqueous acids.[3,11] The particular site of protonation is left undetermined, although it is assumed that protonation occurs at some site on the (dimethylglyoximato)-ligands. The second step in the model, slow on the ^1H n.m.r. time scale, is considered to be removal of pyridine from the cobaloxime as pyridinium trifluoroacetate and its replacement by a co-ordinated trifluoroacetate ligand, to give species (3). This may undergo further protonation on a dimethylglyoximato-ligand.

For the initial rapid equilibrium the observed shift in resonating frequency, $\delta_{obs.}$, is given by [3] equation (2)

$$\delta_{obs.} = ([A]\delta_A + [HA]\delta_{HA})/([A] + [HA]) \quad (2)$$

where [A] and [HA] are the total analytical concentrations of species (1) and (2) in equilibrium respectively, and δ_A and δ_{HA} are the limiting shifts of these species respectively. The value of δ_A is obtained from the ^1H n.m.r. spectrum of the neutral alkyl(pyridine)cobaloxime. Hydrogen-1 n.m.r. spectra of the acidified cobaloxime, when no further shifts are observed, give δ_{HA}. The slow (on the ^1H n.m.r. time scale) conversion (2)→(3) has the effect of removing cobalt-containing material [as (3)]. Because the stoicheiometry of the reaction (2)→(3) produces 1 mol of pyridinium trifluoroacetate for every mol of (3) formed, the concentration of (3) is estimated from the integrated intensity of the pyridinium trifluoroacetate peaks at δ 8.05, 8.55, and 8.80 p.p.m.

The formation constant, K, of (2) from (1c; R = $CHCl_2$) was thus estimated, the shifts being measured relative to that of CH_2Cl_2, which was assumed to be invariant under the conditions described. The values obtained are given in Table 3.

TABLE 3

Values obtained for formation constant K, of (2) from (1c; R = $CHCl_2$)

Total cobalt concentration/ mol dm^{-3}	K/dm^3 mol^{-1}
0.221	3.5 ± 0.7
0.165	3.3 ± 1.0
0.111	3.7 ± 1.0

The relatively large standard deviations are caused by the considerable uncertainties in the measured integrals and to a lesser extent by those of the measured chemical shifts. The values of K found are of approximately the same magnitude as the K found for the monoprotonation of other alkylcobaloximes [3,11] in aqueous solvents. This observation suggests that the initial protonation (1)→(2) probably occurs at a site of the chelating dimethylglyoximato-ligands, most likely on one of the oxygen atoms. There is evidence from i.r. spectroscopy [12] to suggest that protonation of alkylcobaloximes occurs at an oxygen atom of a dimethylglyoximato-residue.

A study of the reaction of dichloromethyl(pyridine)-cobaloxime with tfa by ^{19}F n.m.r. spectroscopy was attempted with the aim of identifying separate resonances from the various fluorine-containing species suggested. However, at room temperature the system was presumably in rapid exchange on the ^{19}F n.m.r. time scale because only a single very broad resonance was observed. This shifted to a small extent upon incremental addition of tfa to the alkyl(pyridine)cobaloxime.

For additions of tfa to alkyl(pyridine)cobaloximes such that [tfa]/[cobalt] > 10 appreciable broadening of the ^1H n.m.r. spectra occurs. A red crystalline solid is deposited from chloroform solution over a period of days to several weeks. This crystalline complex has been identified by single-crystal X-ray diffraction

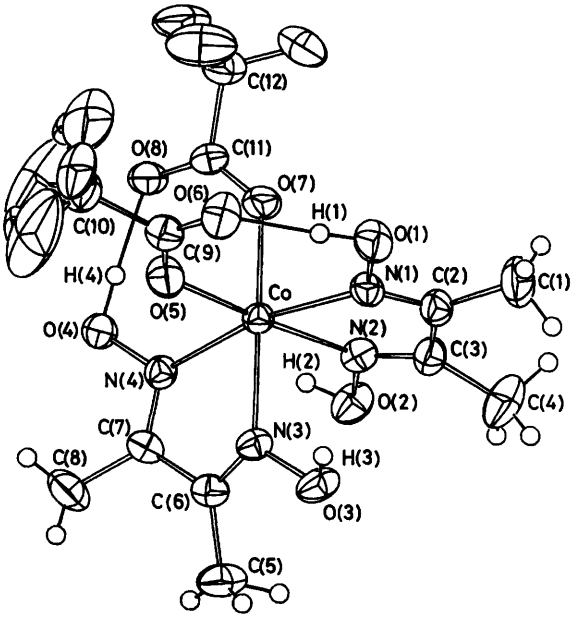
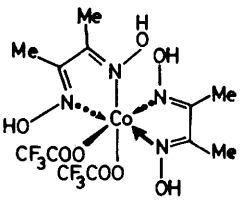


FIGURE 3 View of the molecule, showing the atomic numbering and the internal hydrogen bonds

studies as a mononuclear *cis*-cobaloxime, *cf.* Figure 3 and structure (4).

cis-*Bis*(*butane*-2,3-*dione dioxime*)*bis*(*trifluoroacetoxy*)-*cobalt*(II).—The most significant and initially unexpected feature of the structure (Figure 3) is that the compound is a *cis*-cobaloxime. The complete location of the mole-

cular hydrogen atoms allows a reason for this to be suggested. Trifluoroacetic acid is sufficiently strong as an acid to force dimethylglyoxime residues to be neutral, rather than uninegative as normally found in complexes. As a result, the classic hydrogen-bonded *trans*-dimethylglyoxime geometry is impossible. Instead, intramolecular hydrogen bonds are formed between the free



(4)

oxygen atoms (C=O) of the trifluoroacetate ions and two of the OH groups; these are normal in length (O · · · O 2.63 Å), rather than the very short bonds found in *trans*-dimethylglyoxime complexes.[13] The other two OH groups are involved in intermolecular hydrogen bonds, which link the molecules into infinite chains in the *c* direction (*cf.* Figure 4). These are also of normal

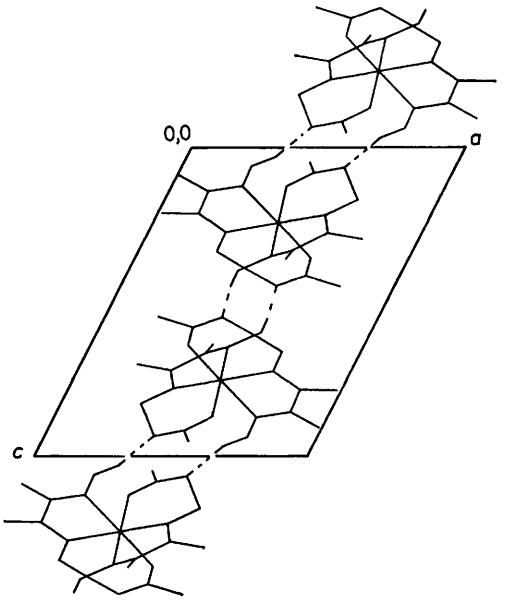


FIGURE 4 Molecular packing, viewed down *b*. For clarity the chloroform, the fluorine atoms, and methyl hydrogen atoms are omitted. The hydrogen bonds are shown as broken lines

length (2.70 and 2.76 Å). The chloroform molecules lie between the chains. The dimensions of the dimethylglyoxime units are similar to those of dimethylglyoximato-units in *trans*-cobaloximes.[13] However, the N–Co distances (*ca.* 2.14 Å) are longer than those (*ca.* 1.9 Å) in typical *trans*-cobaloximes,[13] reflecting the different oxidation states of cobalt.

The *cis*-cobaloxime (4) is formally cobaloxime(II). Magnetic susceptibility measurements give values of $\chi_m = 8\,350 \times 10^{-6}$ c.g.s. units and $\mu_{eff.} = 4.45\ \mu_B$ at 297 K indicating a high-spin cobalt(II) species. Mulls of (4) in Nujol and hexachlorobuta-1,3-diene show i.r. spectra with broad peaks at *ca.* 3 180 and 2 860 cm^{-1} characteristic of strong hydrogen bonding of OH groups. There are characteristic C–F stretching bands at 1 000—1 300 cm^{-1}. Remarkably, (4) is a very stable molecule and can be stored in air without significant oxidation to cobalt(III), in contrast to the behaviour of diaquocobaloxime(II) which is rapidly oxidised in air.

Cobaloximes with a *cis* spatial orientation of the dimethylglyoximate chelates have been reported by Ablov *et al.*[14] Thus, *trans*-aquabis(butane-2,3-dione dioximato)hydroxocobalt(II) was converted by 50% aqueous potassium hydroxide into a dark red complex,[14,15] subsequently shown by *X*-ray study [16] to be a binuclear *cis*-cobaloxime(III), apparently containing neutral, mono-, and di-deprotonated dimethylglyoxime ligands. The formation of this cobaloxime occurs under conditions of extreme (high) pH which presumably disturbs the bis(dimethylglyoximato)-system by deprotonation. The formation of *cis*-cobaloxime (4) also requires extreme (low) pH which disturbs the dimethylglyoximato-system by protonation.

The formation of *cis*-cobaloxime (4) may occur in the following manner from species (3) (*cf.* Scheme). Complex (3) undergoes slow homolysis of its Co–C bond either spontaneously or induced by further protonation from tfa. The resulting cobaloxime(II) is kinetically labile and can add a trifluoroacetate ligand and reorganise from *trans*-bis(dimethylglyoximato) to the *cis* configuration. The rearrangement could occur either by a dissociation of one arm of a dimethylglyoxime or by a twist mechanism. The alkyl ligand R released as an organic radical removes a hydrogen atom from tfa to form RH. The formation of CH_2Cl_2 from dichloromethyl(pyridine)-cobaloxime was detected by ^1H n.m.r. spectroscopy. The production of propane from isopropyl(pyridine)-cobaloxime was demonstrated by g.l.c. The exact sequence of loss of R, co-ordination of a second trifluoroacetate ligand, and various geometrical rearrangements cannot be defined.

We thank the S.R.C. for financial support, Dr. E. Curzon for preliminary work on the crystal structure, and Dr. M. D. Johnson for helpful discussions.

[1/1025 *Received*, 26*th June*, 1981]

REFERENCES

[1] M. P. Atkins, B. T. Golding, D. A. Howes, and P. J. Sellars, *J. Chem. Soc., Chem. Commun.*, 1980, 207.
[2] G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1966, **88**, 3738.
[3] B. T. Golding, T. J. Kemp, P. J. Sellars, and E. Nocchi, *J. Chem. Soc., Dalton Trans.*, 1977, 1266.
[4] A. Bury, M. R. Ashcroft, and M. D. Johnson, *J. Am. Chem. Soc.*, 1978, **100**, 3217.
[5] M. P. Atkins, B. T. Golding, A. Bury, M. D. Johnson, and P. J. Sellars, *J. Am. Chem. Soc.*, 1980, **102**, 3630.
[6] M. P. Atkins, B. T. Golding, and P. J. Sellars, *J. Chem. Soc., Chem. Commun.*, 1978, 954; in ' Vitamin B_{12},' eds. B. Zagalak and W. Friedrich, W. de Gruyter, Berlin, 1979, p. 587.
[7] N. W. Alcock, M. P. Atkins, E. H. Curzon, B. T. Golding, and P. J. Sellars, *J. Chem. Soc., Chem. Commun.*, 1980, 1238.

[8] G. N. Schrauzer, *Inorg. Synth.*, 1969, **11**, 61.
[9] N. W. Alcock, in ' Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970.
[10] J. M. Stewart, Technical Report TR-446, Computer Science Centre, University of Maryland, 1976.
[11] A. Adin and J. H. Espenson, *Chem. Commun.*, 1971, 653; J. H. Espenson and J.-T. Chen, *J. Am. Chem. Soc.*, 1981, **103**, 2036 and refs. cited therein.
[12] A. L. Crumbliss, J. T. Bowman, P. L. Gaus, and A. R. McPhail, *J. Chem. Soc., Chem. Commun.*, 1973, 415.
[13] A. Bigotto, E. Zangrando, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1976, 96 and refs. cited therein.
[14] A. V. Ablov, M. P. Filippov, and N. M. Samus, *Dokl. Akad. Nauk SSSR*, 1960, **133**, 575; A. V. Ablov, N. M. Samus, and O. A. Bologa, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1963, **8**, 440.
[15] A. V. Ablov, Y. A. Siminov, S. T. Malinovskii, O. A. Bologa, and T. I. Malinovskii, *Dokl. Akad. Nauk SSSR*, 1975, **221**, 605.
[16] S. T. Malinovskii, Y. A. Siminov, A. V. Ablov, T. I. Malinovskii, I. D. Samus, and O. A. Bologa, *Dokl. Akad. Nauk SSSR*, 1977, **232**, 326.