

Table 2. Selected bond distances (Å) and bond angles (°)

Ru—N(2)	2.03 (2)	N(7)—C(6)	1.34 (4)
Ru—N(13)	2.11 (2)	N(7)—C(8)	1.34 (4)
Ru—N(20)	2.04 (2)	C(8)—C(9)	1.32 (5)
Ru—N(26)	2.05 (2)	C(9)—C(10)	1.35 (5)
Ru—N(40)	2.06 (2)	C(10)—C(11)	1.39 (5)
Ru—N(46)	2.04 (2)	C(6)—C(11)	1.38 (4)
N(1)—N(2)	1.35 (3)	N(13)—C(12)	1.35 (4)
N(1)—C(5)	1.34 (3)	N(13)—C(14)	1.33 (4)
N(2)—C(3)	1.34 (4)	C(14)—C(15)	1.36 (4)
N(4)—C(5)	1.36 (4)	C(15)—C(16)	1.35 (4)
N(4)—C(3)	1.33 (3)	C(16)—C(17)	1.36 (5)
C(5)—C(6)	1.46 (4)	C(17)—C(12)	1.38 (4)
C(3)—C(12)	1.45 (4)		
N(1)...O(60)	3.14 (7)	N(7)...O(60)	3.29 (7)
N(2)—Ru—N(13)	78 (1)	N(20)—Ru—N(40)	97.2 (9)
N(2)—Ru—N(20)	95 (1)	N(26)—Ru—N(40)	88.6 (9)
N(2)—Ru—N(40)	97.0 (9)	N(26)—Ru—N(46)	97.3 (9)
N(2)—Ru—N(46)	90.4 (9)	N(40)—Ru—N(46)	79 (1)
N(13)—Ru—N(20)	88.2 (9)	N(2)—Ru—N(26)	172.0 (9)
N(13)—Ru—N(26)	96.9 (9)	N(13)—Ru—N(40)	173 (1)
N(13)—Ru—N(46)	96.0 (9)	N(20)—Ru—N(46)	174 (1)
N(20)—Ru—N(26)	79 (1)		

the two bipyridine ligands and the bpt ligand are 78.8, 79.2 and 77.9°, respectively, in agreement with other ruthenium bipyridine compounds (Rillema, Jones & Levy, 1979; Heeg, Kroener & Deutsch, 1985).

The packing of the cations (Fig. 2) is such that bipyridyl ligands in adjacent molecules are roughly

parallel; the shortest C...C contact between such parallel bpy ligands is 3.64 Å. The shortest intermolecular distance in the structure is 2.05 Å between F(1B) and H(16), and the shortest H...H contact is 2.43 Å involving H(15) and H(29).

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Structure of (Methyl 5-deoxy-β-D-ribofuranos-5-yl)(pyridine)cobaloxime Monohydrate

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Abstract. C₁₉H₃₀CoN₅O₈·H₂O, *M_r* = 533.4, monoclinic, *P*2₁, *a* = 8.519 (1), *b* = 17.012 (3), *c* = 9.135 (1) Å, β = 117.04 (1)°, *V* = 1179.2 Å³, *Z* = 2, *D_x* = 1.502 Mg m⁻³, *F*(000) = 560, λ(Mo *K*α) = 0.71073 Å, μ = 0.78 mm⁻¹, *R* = 0.026 for 4022 unique observed reflections, absolute structure determined from anomalous-scattering effects. Co is octahedrally coordinated by two dimethylglyoximate [2,3-butanedione dioximate(1-)], one pyridine and the ribosyl ligands. The Co—C bond length of 2.015 (2) Å and Co—C—C angle of 123.0 (2)° closely resemble those of the vitamin B₁₂ coenzyme adenosylcobalamin, for which this simpler complex is a model.

Introduction. Attempts to elucidate the mechanism of action of vitamin B₁₂ have involved various model

compounds, mainly cobalamins and cobaloximes (Zagalak & Friedrich, 1979; Dolphin, 1982; Golding & Rao, 1987). Among the structural investigations, a coenzyme form of vitamin B₁₂, adenosylcobalamin (AdoCbl), shows a Co—C—C angle of 124° (Lenhert, 1968; Savage, Lindley, Finney & Timmins, 1987). This is rather larger than for other alkylcobalamins, and has been considered to be exceptional, and a sign of strain in the molecule, facilitating cleavage of the Co—C bond in the biological action of the coenzyme (Alcock, Dixon & Golding, 1985; Pett, Liebman, Murray-Rust, Prasad & Glusker, 1987). On the other hand, a wide range of values for the Co—C—C angle is found in alkylcobaloximes, and the variation has been ascribed to steric repulsions between the alkyl substituents and the dimethylglyoximate (dmg) ligands (Bresciani-Pahor,

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

$U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
Co	5042.0 (2)	5000	6418.2 (2)	241 (1)
N(11)	6863 (2)	5720.5 (9)	6765 (2)	301 (5)
N(12)	5511 (2)	4676.4 (9)	4682 (2)	288 (5)
O(11)	7459 (2)	6250.7 (9)	7987 (2)	412 (5)
O(12)	4668 (2)	4067.8 (9)	3702 (2)	406 (5)
C(11)	7524 (2)	5682 (1)	5730 (2)	330 (6)
C(12)	6738 (2)	5058 (1)	4507 (2)	318 (5)
C(13)	8954 (3)	6217 (2)	5805 (3)	532 (9)
C(14)	7319 (3)	4869 (1)	3231 (3)	464 (8)
N(21)	4626 (2)	5294 (1)	8208 (2)	303 (5)
N(22)	3262 (2)	4262.7 (9)	6133 (2)	302 (5)
O(21)	5513 (2)	5884.1 (9)	9274 (2)	422 (5)
O(22)	2719 (2)	3704.3 (9)	4955 (2)	397 (5)
C(21)	3374 (2)	4938 (1)	8363 (2)	345 (6)
C(22)	2577 (2)	4306 (1)	7141 (2)	337 (6)
C(23)	2805 (3)	5129 (2)	9652 (3)	532 (9)
C(24)	1218 (3)	3759 (2)	7134 (3)	514 (9)
N(31)	3156 (2)	5782.0 (9)	4864 (2)	318 (5)
C(31)	1976 (3)	5555 (1)	3363 (3)	407 (7)
C(32)	720 (3)	6056 (2)	2239 (3)	504 (9)
C(33)	682 (3)	6829 (1)	2695 (3)	536 (9)
C(34)	1875 (3)	7069 (1)	4244 (4)	575 (10)
C(35)	3094 (3)	6532 (1)	5292 (3)	451 (8)
C(41)	6872 (2)	4191 (1)	7727 (2)	306 (6)
C(42)	7301 (2)	3974 (1)	9465 (2)	297 (6)
C(43)	8978 (2)	3463 (1)	10220 (2)	333 (6)
C(44)	8596 (3)	2852 (1)	11241 (3)	414 (8)
C(45)	6637 (3)	2746 (1)	10193 (3)	447 (8)
C(46)	4704 (4)	2075 (2)	7760 (4)	711 (12)
O(41)	5949 (2)	3506.6 (9)	9580 (2)	412 (5)
O(42)	10471 (2)	3935 (1)	11115 (2)	487 (6)
O(43)	8956 (2)	3145 (1)	12812 (2)	554 (7)
O(44)	6459 (3)	2224 (1)	8935 (3)	575 (7)
O(5)	6979 (3)	7840 (1)	8608 (4)	733 (10)

Marzilli, Randaccio, Toscano & Zangrando, 1984; Summers, Marzilli, Bresciani-Pahor & Randaccio, 1984).

In order to gain further information concerning the Co—C—C angle in AdoCbl, two closely related compounds have been synthesized, in which the adenosyl group is replaced by a simpler ribosyl substituent, without the adenine group (Anderson, 1988). Methyl 5-deoxy- β -D-ribofuranos-5-ylcobalamin (RibCbl) and the corresponding ribosyl(pyridine)cobaloxime RibCbx show marked similarities to each other and to AdoCbl with respect to the ribosyl moiety in molecular-modelling trials (with *Chem-X*; Davies, 1986). Although we have been unable so far to obtain suitable single crystals of RibCbl for structure determination, we report here the structure of RibCbx and a comparison of it with that of AdoCbl.

Experimental. The compound was prepared by sodium borohydride reduction of bromo(pyridine)cobaloxime, followed by treatment with methyl 5-deoxy-5-iodo- β -D-ribofuranoside in ethanol and extraction of the product from aqueous solution into dichloromethane, and was recrystallized from dichloromethane/petrol (Anderson, 1988).

Crystal size 0.27 \times 0.42 \times 0.54 mm, in Lindemann capillary, Siemens AED2 diffractometer, $T = 295$ K. Unit-cell parameters from 2θ values of 32 reflections (20 – 25°) measured at $\pm\omega$. Data collection in ω/θ scan

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Co—N(11)	1.888 (2)	Co—N(12)	1.885 (2)
Co—N(21)	1.891 (2)	Co—N(22)	1.892 (2)
Co—N(31)	2.072 (2)	Co—C(41)	2.015 (2)
N(11)—O(11)	1.342 (2)	N(11)—C(11)	1.303 (3)
N(12)—O(12)	1.343 (2)	N(12)—C(12)	1.301 (3)
O(11)—H(1)	1.612 (90)	O(12)—H(2)	1.329 (68)
C(11)—C(12)	1.464 (3)	C(11)—C(13)	1.496 (4)
C(12)—C(14)	1.493 (4)	N(21)—O(21)	1.363 (2)
N(21)—C(21)	1.289 (3)	N(22)—O(22)	1.350 (2)
N(22)—C(22)	1.297 (3)	O(21)—H(1)	0.898 (48)
O(22)—H(2)	1.163 (69)	C(21)—C(22)	1.475 (3)
C(21)—C(23)	1.498 (4)	C(22)—C(24)	1.483 (4)
N(31)—C(31)	1.337 (2)	N(31)—C(35)	1.343 (3)
C(31)—C(32)	1.388 (3)	C(32)—C(33)	1.384 (4)
C(33)—C(34)	1.377 (4)	C(34)—C(35)	1.388 (3)
C(41)—C(42)	1.503 (3)	C(42)—C(43)	1.542 (3)
C(42)—O(41)	1.443 (3)	C(43)—C(44)	1.528 (3)
C(43)—O(42)	1.409 (2)	C(44)—C(45)	1.510 (3)
C(44)—O(43)	1.415 (3)	C(45)—O(41)	1.425 (3)
C(45)—O(44)	1.404 (3)	C(46)—O(44)	1.411 (3)
O(42)—H(42O)	0.765 (35)	O(43)—H(43O)	0.703 (59)
N(11)—Co—N(12)	81.9 (1)	N(11)—Co—N(21)	98.4 (1)
N(12)—Co—N(21)	177.9 (1)	N(11)—Co—N(22)	178.2 (1)
N(12)—Co—N(22)	98.8 (1)	N(21)—Co—N(22)	80.9 (1)
N(11)—Co—N(31)	91.2 (1)	N(12)—Co—N(31)	90.3 (1)
N(21)—Co—N(31)	91.8 (1)	N(22)—Co—N(31)	90.5 (1)
N(11)—Co—C(41)	89.4 (1)	N(12)—Co—C(41)	84.1 (1)
N(21)—Co—C(41)	93.8 (1)	N(22)—Co—C(41)	89.1 (1)
N(31)—Co—C(41)	174.3 (1)	Co—N(11)—O(11)	123.2 (2)
Co—N(11)—C(11)	116.0 (1)	O(11)—N(11)—C(11)	120.8 (2)
Co—N(12)—O(12)	122.2 (1)	Co—N(12)—C(12)	116.6 (1)
O(12)—N(12)—C(12)	121.2 (2)	N(12)—O(12)—H(2)	102.1 (24)
N(11)—C(11)—C(12)	113.0 (2)	N(11)—C(11)—C(13)	123.2 (2)
C(12)—C(11)—C(13)	123.8 (2)	N(12)—C(12)—C(11)	112.5 (2)
N(12)—C(12)—C(14)	123.9 (2)	C(11)—C(12)—C(14)	123.6 (2)
O(11)—H(1)—O(21)	175.2 (50)	Co—N(21)—O(21)	123.5 (2)
Co—N(21)—C(21)	117.5 (1)	O(21)—N(21)—C(21)	119.0 (2)
Co—N(22)—O(22)	122.6 (2)	Co—N(22)—C(22)	117.1 (1)
O(22)—N(22)—C(22)	120.3 (2)	N(21)—O(21)—H(1)	99.5 (23)
N(22)—O(22)—H(2)	101.6 (26)	N(21)—C(21)—C(22)	112.2 (2)
N(21)—C(21)—C(23)	124.4 (2)	C(22)—C(21)—C(23)	123.4 (2)
N(22)—C(22)—C(21)	112.2 (2)	N(22)—C(22)—C(24)	124.3 (2)
C(21)—C(22)—C(24)	123.4 (2)	O(12)—H(2)—O(22)	171.8 (50)
Co—N(31)—C(31)	120.3 (1)	Co—N(31)—C(35)	122.1 (1)
C(31)—N(31)—C(35)	117.6 (2)	N(31)—C(31)—C(32)	123.3 (2)
C(31)—C(32)—C(33)	118.5 (2)	C(32)—C(33)—C(34)	118.9 (2)
C(33)—C(34)—C(35)	119.0 (2)	N(31)—C(35)—C(34)	122.8 (2)
Co—C(41)—C(42)	123.0 (2)	C(41)—C(42)—C(43)	110.0 (2)
C(41)—C(42)—O(41)	113.2 (1)	C(43)—C(42)—O(41)	105.3 (1)
C(42)—C(43)—C(44)	104.2 (2)	C(42)—C(43)—O(42)	110.3 (2)
C(44)—C(43)—O(42)	114.8 (2)	C(43)—C(44)—C(45)	100.1 (2)
C(43)—C(44)—O(43)	111.8 (2)	C(45)—C(44)—O(43)	110.7 (2)
C(44)—C(45)—O(41)	106.2 (2)	C(44)—C(45)—O(44)	105.8 (2)
O(41)—C(45)—O(44)	112.4 (2)	C(42)—O(41)—C(45)	109.3 (2)
C(43)—O(42)—H(42O)	113.1 (23)	C(44)—O(43)—H(43O)	119.8 (79)
C(45)—O(44)—C(46)	114.8 (3)		

mode with on-line profile fitting (Clegg, 1981), $2\theta_{max}$ 50° , three quadrants of data ($+h, k, l$; $+h, -k, -l$; $+h, -k, l$) with $|h|_{max}$ 10, $|k|_{max}$ 20, $|l|_{max}$ 10, no variation in intensity for 3 standard reflections, no absorption or extinction corrections. 6679 reflections measured, 4133 unique (Friedel pairs not averaged), 4022 with $F > 4\sigma_c(F)$ (σ_c from counting statistics only), $R_{int} = 0.025$.

Structure solution by Patterson and difference syntheses, blocked-cascade least-squares refinement on F , $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 2.3 + 6.1G + 1.4G^2 - 6.0S + 4.1S^2 - 9.4GS$ [$G = F_o/F_{max}$, $S = \sin\theta/\sin\theta_{max}$ (Hong & Robertson, 1985)], anisotropic thermal parameters for all non-H atoms, O—H H atoms freely refined, H₂O H atoms not located, C—H H atoms constrained [C—H = 0.96 \AA , H—C—H = 109.5° , aromatic H on ring angle external bisectors, $U(H)$

$= 1.2U_{eq}(C)$, absolute structure confirmed by refinement of $\eta = +1.06(4)$ (Rogers, 1981). $R = 0.026$, $wR = 0.026$ for 338 parameters, goodness-of-fit = 1.12, mean $\Delta/\sigma = 0.019$, max. $\Delta/\sigma = 0.166$, $(\Delta\rho)_{max} = 0.68$, $(\Delta\rho)_{min} = -0.46 \text{ e } \text{Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974); *SHELXTL* (Sheldrick, 1985) and local computer programs.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51477 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

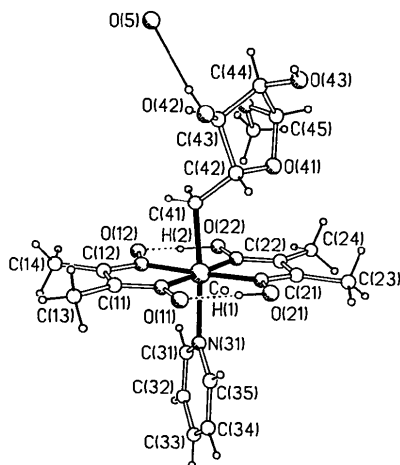


Fig. 1. Structure of RibCbx together with the water molecule, showing the atom-labelling scheme. Atoms not labelled are the dmg N atoms, which take the same numbers as the corresponding O atoms, and the ribosyl methoxy atoms O(44) and C(46).

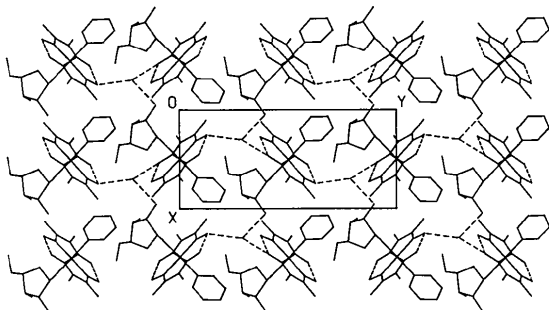


Fig. 2. Parallel projection along the *c* axis, with hydrogen bonds dashed.

Discussion. The molecular structure is shown in Fig. 1. The crystal structure additionally contains one water molecule per RibCbx molecule, presumably derived from the solvent-extraction process during the synthesis and retained in the recrystallization. The water molecule engages in a network of hydrogen bonds to different RibCbx molecules, involving one hydroxyl group of the ribose [$O(5)\cdots O(42)$ 2.784 (5) Å] and two dmg O atoms [$O\cdots O$ 2.830 (5) and 2.844 (5) Å]. The hydrogen bonds, including intramolecular ones between pairs of dmg ligands, are shown dashed in Fig. 2. Although the precision of the H-atom positions is low, both of the intramolecular $O-H\cdots O$ hydrogen bonds appear to be unsymmetrical, and unequally so [$O\cdots O$ 2.508 (4), $O-H$ 0.90 (5), $H\cdots O$ 1.61 (9) Å; $O\cdots O$ 2.485 (4), $O-H$ 1.16 (9), $H\cdots O$ 1.33 (7) Å]. The asymmetry is such as to associate both of the H atoms more closely with the same dmg ligand, so that there is some tendency towards one doubly protonated and one completely unprotonated ligand. The incidence of such a proton distribution in complexes of dmg has been previously discussed (Bresciani-Pahor, Calligaris & Randaccio, 1978; Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985; Elder, Nerone & Barrick, 1980). It is commonly observed when the dmg ligands are involved in additional hydrogen bonding, as is the case here; in the absence of such effects, symmetrical hydrogen bonds may be formed.

In common with other cobalamins and cobaloximes, RibCbx has an octahedrally coordinated Co atom, which lies only 0.031 (1) Å out of the mean plane of the four dmg N atoms [r.m.s. $\Delta = 0.004(1)$ Å], the displacement being away from the α -C atom of the alkyl substituent. The Co—C bond length is normal for such molecules. The Co—C—C angle of 123.0 (2)° is essentially the same as that observed in AdoCbl itself, which has been regarded as abnormal for a cobalamin. This suggests that such a large angle may be a requirement of the ribosyl substituent (with or without the additional adenine group, which lies well away from the Co—C attachment), and that the substitution of dmg ligands for a corrin ring is less important. Thus RibCbx, which is fairly easily prepared and handled, appears to be a particularly good simple model for the vitamin B₁₂ coenzyme AdoCbl. Together with the cobalamin RibCbl, it is being further studied on this basis.

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Structure du Triméthylsilyl-5 [Tris(triméthylsilyl)-1,2,2 éthyl]-2 Phénoxytriméthylsilane

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Abstract. C₂₃H₅₀OSi₅, *M_r* = 483.1, triclinic, *P* $\bar{1}$, *a* = 10.544 (2), *b* = 12.880 (2), *c* = 13.452 (4) Å, α = 108.20 (5), β = 110.50 (5), γ = 94.05 (4)°, *V* = 1592 Å³, *Z* = 2, *D_x* = 1.01 g cm⁻³, $\lambda(\text{Cu } K\alpha)$ = 1.54178 Å, μ = 20.85 cm⁻¹, *F*(000) = 532, room temperature, final *R* = 0.051 for 3571 observed reflections. The bond lengths and angles are normal. The phenyl ring and its substituents are planar. Crystal packing is by weak van der Waals bonds.

Introduction. La silylation réductrice des hétérocycles aromatiques à cinq chaînons, soufré et oxygéné, par les systèmes triméthylchlorosilane, lithium, tétrahydrofurane (Laguerre, Duffaut, Dunoguès & Calas, 1980) ou triméthylchlorosilane, magnésium, hexaméthylphosphorotriamide (Biran, Duffaut, Dunoguès & Calas, 1975) conduit à l'ouverture du cycle accompagnée de la désulfuration totale dans le cas du thiophène; avec le furanne, la réaction est plus difficile mais se fait partiellement, avec désoxygénation. Les composés organosiliciés constituant des synthons très recherchés, il était intéressant d'appliquer cette réaction

au benzothiophène et au benzofuranne pour lesquels la silylation du noyau benzénique s'ajouterait à la réaction d'ouverture du cycle à cinq chaînons en conduisant à des modèles nouveaux.

Au cours de l'étude de la silylation du benzofuranne, nous avons isolé le composé cité en titre et afin de confirmer sa structure relativement inattendue nous avons entrepris son étude cristallographique.

Partie expérimentale. De petits cristaux transparents ont été obtenus par lent refroidissement d'une solution dans le méthanol. Dimensions du cristal 0,1 × 0,06 × 0,3 mm. Diffractomètre Enraf-Nonius CAD-4, Cu *K* α radiation, monochromateur graphite, λ = 1,54178 Å, paramètres cristallins déterminés par moindres carrés à partir de 25 réflexions: 16° < 2 θ < 40°, mesures par balayage ω -2 θ , largeur de balayage (2,4 + 0,15 tg θ)°, largeur d'ouverture de la fenêtre (2,5 + 1 tg θ) mm, contrôles d'intensité toutes les 5400 s effectués sur deux réflexions, corrections des facteurs de Lorentz et polarisation, absorption négligée à cause de la petite dimension du cristal, 4735 réflexions mesurées dont 3571 ob-