

Tables 1 and 2.* Fig. 1, prepared using ORTEPII (Johnson, 1976), shows details of the cation structure and copper coordination.

Discussion. The copper coordination geometry is distorted octahedral with longer bonds to the axial O(12) and S(1) atoms. The macrocyclic ring adopts a rather strained [333] conformation (Dale, 1973, 1974; Boeyens & Dobson, 1987) as evidenced in the 'non-ideal' torsional angles about C(6) (Fig. 1). The alternative [234] conformation is energetically less stable by about 12–20 kJ mol⁻¹ (Dobson, 1986) but may be preferred by those metal ions which do not accept facial symmetrical coordination – such as Cu^{II} and Pt^{II}. Related macrocyclic Cu^{II} complexes with the unfunctionalized nine-membered N₂S ligand have been reported (Dobson, 1986; Boeyens, Dobson & Hancock, 1985) in both of which the macrocycle adopts a [234] conformation. This [234] con-

formation is common for mixed-donor nine-membered macrocyclic ligands that may interact asymmetrically with metal ions that cannot accept symmetrical facial coordination.

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* Lists of structure factors, thermal parameters, calculated H-atom coordinates and all torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51978 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of *trans*-Cyanobis(dimethylglyoximato)pyridinecobalt(III) Hemihydrate and *trans*-Cyclohexylbis(dimethylglyoximato)(1,5,6-trimethylbenzimidazole)cobalt(III)

BY W. M. ATTIA,* E. ZANGRANDO AND L. RANDACCIO†

Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy

L. ANTOLINI

Dipartimento di Chimica, Università di Modena, 41100 Modena, Italy

AND C. LOPEZ

Department de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Barcelona, Spain

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Abstract. (I) [Co(CN)(C₄H₇N₂O₂)₂(C₅H₅N)].0.5H₂O, *M_r* = 403.3, monoclinic, *P*2₁/*m*, *a* = 7.564 (1), *b* = 13.950 (1), *c* = 8.653 (1) Å, β = 98.20 (1)°, *V* = 903.7 (3) Å³, *Z* = 2, *D_x* = 1.48 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 9.2 cm⁻¹, *F*(000) = 418, *T* = 295 (1) K, *R* = 0.027 for 1815 unique observed

reflections. (II) [Co(C₆H₁₁)(C₄H₇N₂O₂)₂(C₁₀H₁₂N₂)], *M_r* = 532.5, monoclinic, *P*2₁/*n*, *a* = 17.133 (2), *b* = 8.566 (1), *c* = 19.369 (3) Å, β = 115.36 (3)°, *V* = 2568.6 (9) Å³, *Z* = 4, *D_x* = 1.37 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 7.0 cm⁻¹, *F*(000) = 1128, *T* = 295 (1) K, *R* = 0.044 for 3290 unique observed reflections. The axial fragment of the distorted octahedral polyhedron of Co is characterized by Co—C and Co—N distances of 1.995 (2) and 1.937 (2) Å in

* On leave from the Physics Department, Suez Canal University, Ismailia, Egypt.

† To whom correspondence should be addressed.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters for pyCo(DH)₂CN.0.5H₂O
$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co	0.12921 (4)	0.25	0.20692 (3)	2.01 (1)
O(1)	-0.1577 (2)	0.3392 (1)	0.3321 (2)	3.70 (5)
O(2)	0.4103 (2)	0.3388 (1)	0.0730 (2)	3.40 (5)
N(1)	-0.0086 (2)	0.3534 (1)	0.2670 (2)	2.66 (5)
N(2)	0.2645 (2)	0.3529 (1)	0.1425 (2)	2.51 (5)
N(3)	0.2781 (2)	0.25	0.4168 (2)	2.27 (6)
N(4)	-0.0853 (3)	0.25	-0.1145 (3)	3.84 (9)
C(1)	-0.0466 (4)	0.5278 (2)	0.2809 (3)	5.0 (1)
C(2)	0.0469 (3)	0.4387 (1)	0.2424 (2)	3.04 (6)
C(3)	0.2103 (3)	0.4384 (1)	0.1683 (2)	3.12 (7)
C(4)	0.3033 (4)	0.5268 (2)	0.1273 (4)	5.4 (1)
C(5)	-0.0130 (3)	0.25	0.0021 (3)	2.34 (7)
C(6)	0.2021 (3)	0.25	0.5476 (3)	2.75 (7)
C(7)	0.3009 (3)	0.25	0.6942 (3)	3.19 (8)
C(8)	0.4839 (4)	0.25	0.7092 (3)	3.16 (8)
C(9)	0.5616 (4)	0.25	0.5761 (3)	4.3 (1)
C(10)	0.4564 (3)	0.25	0.4323 (3)	3.9 (1)
OW	0.412 (2)	0.5048 (9)	0.517 (2)	13 (1)

(I) and of 2.105 (2) and 2.073 (3) Å in (II). The equatorial ligands (DH₂) are essentially coplanar in (I), but their mean planes make a dihedral angle of 10.8 (5)° in (II), bending towards the Me₃Bzm ligand.

Introduction. Alkylcobaloximes, LCo(DH)₂R complexes, where DH = monoanion of dimethylglyoxime, L = neutral Lewis base and R = alkyl group, have been widely studied as simple models of the vitamin B₁₂ system (Halpern, 1985). On the other hand, they have been shown to be a flexible class of compounds for studying the interrelationship between steric and electronic effects depending upon the nature of the axial L and R ligands (Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985). In fact, a large variety of complexes having different R and L axial ligands have been prepared and studied both in solution and in the solid state (Marzilli, Bayo, Summers, Thomas, Zangrando, Bresciani-Pahor, Mari & Randaccio, 1987). For the series having L = py many complexes with different R groups have been structurally characterized. However, the structure of the cyano derivative which has the same axial R group as vitamin B₁₂ had so far not been determined. Recently the systematic structural study has been extended to other series, such as that having L = 1,5,6-trimethylbenzimidazole (Me₃Bzm) (Bresciani-Pahor, Attia, Randaccio, Lopez & Charland, 1987). Therefore, we report the structure of pyCo(DH)₂CN (I) and Me₃BzmCo(DH)₂Chx (II), where Chx = cyclohexyl.

Experimental. The synthesis and crystallization of the two complexes were performed with usual techniques (Bresciani-Pahor *et al.*, 1985) and will be published elsewhere. Orange-red crystals having approximate

Table 2. Final fractional coordinates and equivalent isotropic thermal parameters for Me₃BzmCo(DH)₂Chx

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{1}{3}(a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3))$.

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co	0.06885 (3)	0.08557 (6)	0.33842 (2)	2.307 (8)
O(1)	0.1089 (2)	-0.1192 (4)	0.2422 (1)	4.06 (7)
O(2)	-0.0431 (2)	0.0326 (4)	0.4090 (1)	3.88 (6)
O(3)	0.0381 (2)	0.2855 (4)	0.4425 (2)	4.42 (7)
O(4)	0.1751 (2)	0.1423 (4)	0.2619 (1)	4.12 (7)
N(1)	0.0644 (2)	-0.0974 (4)	0.2841 (2)	2.79 (6)
N(2)	-0.0110 (2)	-0.0250 (4)	0.3624 (2)	2.74 (6)
N(3)	0.0794 (2)	0.2665 (4)	0.3966 (2)	3.12 (7)
N(4)	0.1476 (2)	0.1959 (4)	0.3126 (2)	3.11 (7)
N(5)	0.1674 (2)	-0.0173 (4)	0.4352 (2)	2.67 (6)
N(6)	0.2214 (2)	-0.1456 (4)	0.5456 (2)	2.82 (7)
C(1)	0.0103 (3)	-0.3645 (5)	0.2534 (3)	4.8 (1)
C(2)	0.0171 (2)	-0.2103 (5)	0.2902 (2)	3.16 (9)
C(3)	-0.0265 (2)	-0.1677 (5)	0.3371 (2)	3.15 (9)
C(4)	-0.0819 (3)	-0.2790 (6)	0.3572 (3)	5.5 (1)
C(5)	0.1558 (4)	0.5120 (6)	0.4456 (3)	5.9 (2)
C(6)	0.1355 (3)	0.3688 (5)	0.3978 (2)	3.7 (1)
C(7)	0.1754 (2)	0.3278 (5)	0.3471 (2)	3.8 (1)
C(8)	0.2419 (3)	0.4263 (7)	0.3371 (3)	6.3 (1)
C(9)	-0.0302 (2)	0.1900 (5)	0.2456 (2)	2.66 (8)
C(10)	-0.0631 (2)	0.0933 (5)	0.1733 (2)	3.46 (9)
C(11)	-0.1318 (3)	0.1796 (6)	0.1050 (2)	4.5 (1)
C(12)	-0.2070 (3)	0.2310 (6)	0.1216 (3)	4.2 (1)
C(13)	-0.1744 (3)	0.3291 (6)	0.1933 (3)	4.2 (1)
C(14)	-0.1062 (2)	0.2411 (5)	0.2614 (2)	3.49 (9)
C(15)	0.1545 (2)	-0.0646 (5)	0.4945 (2)	2.81 (8)
C(16)	0.2836 (2)	-0.1525 (4)	0.5182 (2)	2.62 (8)
C(17)	0.3639 (2)	-0.2236 (5)	0.5465 (2)	3.13 (9)
C(18)	0.4120 (2)	-0.2101 (5)	0.5050 (2)	3.28 (9)
C(19)	0.3790 (2)	-0.1260 (5)	0.4353 (2)	3.09 (8)
C(20)	0.2981 (2)	-0.0575 (5)	0.4075 (2)	3.19 (9)
C(21)	0.2498 (2)	-0.0708 (4)	0.4496 (2)	2.57 (7)
C(22)	0.2256 (3)	-0.2176 (6)	0.6149 (2)	4.1 (1)
C(23)	0.5001 (3)	-0.2863 (6)	0.5342 (3)	4.7 (1)
C(24)	0.4310 (2)	-0.1120 (6)	0.3893 (2)	4.4 (1)

dimensions 0.40 × 0.35 × 0.20 mm (I), 0.50 × 0.35 × 0.20 mm (II). Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo K α , lattice constants by least-squares refinement of the setting angles of 25 reflections [$12 \leq \theta \leq 18^\circ$ (I), $14 \leq \theta \leq 19^\circ$ (II)]. Three standard reflections measured every 4000 s of X-ray exposure [431, 150, 190 for (I) and 638, 449, 653 for (II)], no significant variation noted, $\omega/2\theta$ scan, scan speed 1.3–5.5° min⁻¹ (I) and 1.0–5.0° min⁻¹ (II) in ω , scan width (0.8 + 0.35tan θ) and (1.4 + 0.35tan θ)° for (I) and (II) respectively, in the ranges $1 \leq \theta \leq 28$ and $2.5 \leq \theta \leq 30^\circ$, 4788 and 8128 reflections measured in the ranges $-9 \leq h \leq 9$, $-18 \leq k \leq 18$, $0 \leq l \leq 11$ and $-24 \leq h \leq 24$, $0 \leq k \leq 12$, $0 \leq l \leq 27$ for (I) and (II), respectively. 1815 and 3290 observed reflections [$I > 3\sigma(I)$] for (I) and (II) used for structure determinations, space group from systematic absences, intensities corrected for Lorentz-polarization effects, corrected for absorption via ψ scan, max./min. transmission 1.00/0.93 and 0.998/0.898 respectively. The structures were solved by Patterson method, Fourier synthesis and full-matrix

least squares on F , 177 and 316 parameters refined for the two structures, respectively. The difference map of (I) showed a large peak of height $\sim 1.0 \text{ e } \text{Å}^{-3}$ with a maximum 0.71 Å from an inversion center. This residual was interpreted as due to one water molecule of crystallization with partial site occupancy. Various refinements of the occupancy and of the isotropic thermal parameters of the O atom led to a final occupancy factor of 0.25. Anisotropic temperature factors for all non-H atoms, H atoms isotropically refined for (I) and fixed at calculated positions with $B = 1.3 \times B_{\text{eq}}$ of the corresponding C atom for (II), $R = 0.027$ and 0.044 respectively, $wR = 0.030$ and 0.050 , $S = 1.16$ and 1.14 , function minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1.31/\sigma^2(F) + 0.0003F^2$ for (I) and $w = 1/[\sigma(F_o)^2 + (0.02F_o)^2 + 1]$ for (II), max. $\Delta/\sigma = 0.1$ for (I) and 0.03 for (II), the final difference maps had a max. of 0.36 and $0.60 \text{ e } \text{Å}^{-3}$ and a min. of -0.45 and $-0.35 \text{ e } \text{Å}^{-3}$, respectively, complex neutral-atom scattering factors from *Inter-*

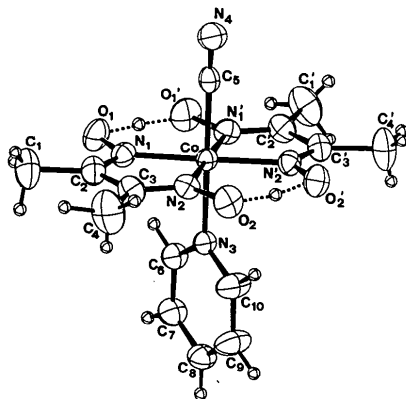


Fig. 1. ORTEP drawing and atom-numbering scheme of compound (I). Primed atoms are related to the unprimed ones by the crystallographic symmetry plane.

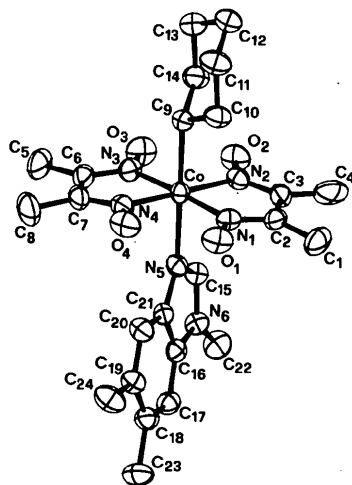


Fig. 2. ORTEP drawing and numbering scheme for non-H atoms of compound (II).

Table 3. Bond distances (Å) and bond angles (°) for $\text{pyCo}(\text{DH})_2\text{CN}\cdot 0.5\text{H}_2\text{O}$

Primed atoms are related to unprimed ones by the symmetry transformation $x, 1-y, z$ of the reference coordinates.

Co—N(1)	1.896 (1)	Co—N(2)	1.893 (1)
Co—N(3)	1.995 (2)	Co—C(5)	1.937 (2)
O(1)—N(1)	1.345 (2)	O(2)—N(2)	1.343 (2)
N(1)—C(2)	1.289 (2)	N(2)—C(3)	1.290 (2)
C(1)—C(2)	1.492 (2)	C(3)—C(4)	1.489 (3)
C(2)—C(3)	1.471 (2)	C(5)—N(4)	1.077 (3)
N(3)—C(6)	1.341 (3)	C(6)—C(7)	1.377 (3)
C(7)—C(8)	1.371 (3)	C(8)—C(9)	1.365 (3)
C(9)—C(10)	1.379 (3)	C(10)—N(3)	1.336 (3)
N(1)—Co—N(2)	81.09 (6)	N(1)—Co—N(1')	99.12 (9)
N(1)—Co—N(2')	178.78 (6)	N(1)—Co—N(3)	90.67 (5)
N(1)—Co—C(5)	89.74 (6)	N(2)—Co—N(2')	98.67 (9)
N(2)—Co—N(3)	90.53 (5)	N(2)—Co—C(5)	89.07 (6)
N(3)—Co—C(5)	179.38 (9)	Co—N(1)—O(1)	121.9 (1)
Co—N(1)—C(2)	116.9 (1)	Co—N(2)—C(3)	116.8 (1)
Co—N(2)—O(2)	122.3 (1)	Co—C(5)—N(4)	176.8 (2)
Co—N(3)—C(6)	121.0 (1)	Co—N(3)—C(10)	121.5 (2)
O(1)—N(1)—C(2)	121.2 (1)	O(2)—N(2)—C(3)	120.9 (1)
N(1)—C(2)—C(1)	123.8 (2)	N(2)—C(3)—C(4)	123.5 (2)
N(1)—C(2)—C(3)	112.5 (1)	N(2)—C(3)—C(2)	112.7 (1)
C(1)—C(2)—C(3)	123.7 (2)	C(4)—C(3)—C(2)	123.8 (2)
C(10)—N(3)—C(6)	117.6 (2)	N(3)—C(6)—C(7)	122.4 (2)
C(6)—C(7)—C(8)	119.6 (2)	C(7)—C(8)—C(9)	118.1 (2)
C(8)—C(9)—C(10)	119.9 (2)	C(9)—C(10)—N(3)	122.4 (2)

national Tables for X-ray Crystallography (1974), no correction for secondary extinction, the calculations were carried out on a Cray X-MP/48 computer using the *SHELX76* (Sheldrick, 1976) program system for (I) and the Enraf-Nonius *SDP* (Frenz, 1983) on a PDP 11/44 for (II).

Discussion. The atomic parameters of non-H atoms of (I) and (II) are listed in Tables 1 and 2.* *ORTEP* drawings (Johnson, 1965) of molecules (I) and (II) with the atom-numbering schemes are depicted in Figs. 1 and 2, respectively. Bond lengths and angles for (I) and (II) are given in Tables 3 and 4. In both complexes, the $(\text{DH})_2$ ligands occupy the four equatorial positions of a distorted octahedron around Co, the axial positions being occupied by the *L* and *R* ligands. The two DH units are approximately planar and make a dihedral angle, α , of $0.2 (4)^\circ$ (I) and $10.8 (5)^\circ$ bending towards Me_3Bzm in (II). The Co atom displacements are 0.02 Å towards py in (I) and 0.02 Å towards C(9) in (II). In the $\text{pyCo}(\text{DH})_2\text{R}$ complexes the Co—py bond lengths vary from $1.973 (4) \text{ Å}$ when $R = \text{N}_3$, to $2.102 (3) \text{ Å}$ when $R = \text{adamantyl}$ (Bresciani-Pahor *et al.*, 1985). The value of $1.995 (2) \text{ Å}$ found in (I) indicates that the σ -donor power of the CN group is close to that of weak

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, atomic parameters for H atoms, and bond lengths and angles involving H atoms for (I) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51957 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Bond distances (Å) and bond angles (°) for Me₃BzmCo(DH)₂Chx

Numbers in parentheses are estimated standard deviations in the least significant digits.

Co—N(1)	1.871 (3)	C(2)—C(3)	1.449 (7)
Co—N(2)	1.879 (3)	C(3)—C(4)	1.508 (7)
Co—N(3)	1.880 (3)	C(5)—C(6)	1.486 (7)
Co—N(4)	1.882 (4)	C(6)—C(7)	1.459 (7)
Co—N(5)	2.105 (2)	C(7)—C(8)	1.496 (8)
Co—C(9)	2.073 (4)	C(9)—C(10)	1.514 (5)
O(1)—N(1)	1.344 (5)	C(9)—C(14)	1.524 (6)
O(2)—N(2)	1.336 (5)	C(10)—C(11)	1.532 (5)
O(3)—N(3)	1.362 (5)	C(11)—C(12)	1.520 (7)
O(4)—N(4)	1.340 (5)	C(12)—C(13)	1.510 (6)
N(1)—C(2)	1.299 (5)	C(13)—C(14)	1.535 (5)
N(2)—C(3)	1.301 (5)	C(16)—C(17)	1.384 (5)
N(3)—C(6)	1.294 (6)	C(16)—C(21)	1.391 (5)
N(4)—C(7)	1.296 (5)	C(17)—C(18)	1.383 (7)
N(5)—C(15)	1.323 (5)	C(18)—C(19)	1.416 (5)
N(5)—C(21)	1.395 (5)	C(18)—C(23)	1.514 (6)
N(6)—C(15)	1.343 (5)	C(19)—C(20)	1.385 (6)
N(6)—C(16)	1.380 (6)	C(19)—C(24)	1.510 (7)
N(6)—C(22)	1.449 (5)	C(20)—C(21)	1.392 (7)
C(1)—C(2)	1.482 (6)		
N(1)—Co—N(2)	81.8 (1)	C(1)—C(2)—C(3)	124.8 (4)
N(1)—Co—N(3)	176.9 (1)	N(2)—C(3)—C(2)	113.3 (4)
N(1)—Co—N(4)	97.6 (1)	N(2)—C(3)—C(4)	123.1 (4)
N(1)—Co—N(5)	88.5 (1)	C(2)—C(3)—C(4)	123.5 (4)
N(1)—Co—C(9)	93.0 (1)	N(3)—C(6)—C(5)	123.0 (5)
N(2)—Co—N(3)	99.2 (2)	N(3)—C(6)—C(7)	112.6 (4)
N(2)—Co—N(4)	179.1 (2)	C(5)—C(6)—C(7)	124.4 (4)
N(2)—Co—N(5)	87.7 (1)	N(4)—C(7)—C(6)	112.5 (5)
N(2)—Co—C(9)	91.1 (1)	N(4)—C(7)—C(8)	123.9 (5)
N(3)—Co—N(4)	81.3 (2)	C(6)—C(7)—C(8)	123.6 (5)
N(3)—Co—N(5)	88.6 (1)	Co—C(9)—C(10)	114.1 (3)
N(3)—Co—C(9)	89.8 (1)	Co—C(9)—C(14)	113.7 (3)
N(4)—Co—N(5)	93.1 (1)	C(10)—C(9)—C(14)	109.4 (3)
N(4)—Co—C(9)	88.1 (1)	C(9)—C(10)—C(11)	112.2 (4)
N(5)—Co—C(9)	178.0 (2)	C(10)—C(11)—C(12)	111.5 (4)
Co—N(1)—O(1)	124.0 (2)	C(11)—C(12)—C(13)	109.9 (3)
Co—N(1)—C(2)	116.7 (3)	C(12)—C(13)—C(14)	111.3 (4)
O(1)—N(1)—C(2)	119.3 (3)	C(9)—C(14)—C(13)	111.7 (4)
Co—N(2)—O(2)	122.3 (2)	N(5)—C(15)—N(6)	113.0 (3)
Co—N(2)—C(3)	115.7 (3)	N(6)—C(16)—C(17)	131.8 (3)
O(2)—N(2)—C(3)	121.7 (4)	N(6)—C(16)—C(21)	105.8 (3)
Co—N(3)—O(3)	123.1 (3)	C(17)—C(16)—C(21)	122.4 (4)
Co—N(3)—C(6)	116.7 (3)	C(16)—C(17)—C(18)	118.2 (3)
O(3)—N(3)—C(6)	119.8 (3)	C(17)—C(18)—C(19)	120.3 (3)
Co—N(4)—O(4)	122.7 (2)	C(17)—C(18)—C(23)	119.6 (4)
Co—N(4)—C(7)	116.6 (3)	C(19)—C(18)—C(23)	120.2 (4)
O(4)—N(4)—C(7)	120.8 (4)	C(18)—C(19)—C(20)	120.7 (5)
Co—N(5)—C(15)	122.3 (2)	C(18)—C(19)—C(24)	120.4 (3)
Co—N(5)—C(21)	132.2 (3)	C(20)—C(19)—C(24)	118.9 (3)
C(15)—N(5)—C(21)	104.9 (3)	C(19)—C(20)—C(21)	119.0 (3)
C(15)—N(6)—C(16)	107.1 (4)	N(5)—C(21)—C(16)	109.1 (3)
C(15)—N(6)—C(22)	126.2 (4)	N(5)—C(21)—C(20)	131.4 (3)
C(16)—N(6)—C(22)	126.6 (3)	C(16)—C(21)—C(20)	119.6 (3)
N(1)—C(2)—C(1)	122.9 (5)		
N(1)—C(2)—C(3)	112.3 (4)		

donor groups, such as N₃. The geometry of the axial fragment in (II) is very close to that found in the *i*-Pr (isopropyl) analogue where the Co—N, Co—C distances and the N—Co—C angle are 2.097 (2), 2.076 (2) Å and 176.41 (8)°, respectively (Charland, Zangrando, Bresciani-Pahor, Randaccio & Marzilli, 1989). This shows that the σ -donor power and the bulk, of cyclohexyl, as measured by the length of the axial Co—N and Co—C bonds, respectively (Bresciani-Pahor *et al.*, 1985), should be very similar to those of *i*-Pr. The Chx ligand has an approximate chair conformation, the Co atom occupying the equatorial position of C(9). The bonding to Co determines a deformation of the cyclohexyl ring, which becomes slightly elongated along the C(9)···C(12) direction. In fact, the angles at C(9) and

Table 5. Comparison of axial Co—C and Co—N bond lengths (Å) in cobalamins and cobaloximes

	Co—C	Co—N	Ref.
CN-cobalamin	1.91 (3)	2.03 (2)	(a)
pyCo(DH) ₂ CN	1.937 (2)	1.995 (2)	(b)
Me-cobalamin	1.99 (2)	2.19 (2)	(c)
pyCo(DH) ₂ Me	1.998 (5)	2.068 (3)	(d)
5'-Adenosylcobalamin	2.00 (1)	2.24 (1)	(e) (X-ray)
	2.04 (1)	2.24 (1)	(e) (neutron)
pyCo(DH) ₂ CH ₂ CMe ₃	2.060 (6)	2.081 (4)	(d)

References: (a) Marzilli, Glusker, Bresciani-Pahor, Randaccio & Zangrando (1985); (b) present work; (c) Rossi, Glusker, Randaccio, Summers, Toscano & Marzilli (1985); (d) Bresciani-Pahor *et al.* (1985); (e) Savage, Lindley, Finney & Timmins (1987).

C(12) are significantly narrower than the other internal angles of the six-membered ring, while the C(10)—C(11) and C(14)—C(13) distances are significantly longer than the others (Table 4). Similar deformations in the geometry of alkyl groups bonded to cobalt have already been observed (Bresciani-Pahor *et al.*, 1985, 1987). A comparison of axial Co—N and Co—C bond lengths in the vitamin B₁₂ system and in simple models is given in Table 5. Making allowances for the lower accuracy of data with respect to cobalamins, the Co—C bond length values are very close in both series depending upon the organic residue bonded to Co. On the other hand, the Co—N bond lengths are significantly shorter in the models, but they follow the same trend in cobalamins and cobaloximes, increasing with the σ -donor power of the *R* group.

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