ELSEVIER

Journal of Organometallic Chemistry 560 (1998) 155–161

Journal of Organometallic Chemistry

Steric *cis* influence and lateral compression of the metallabicycle in bis(dioxime) vitamin B_{12} models

B.D. Gupta [a],*, Kushal Qanungo [a], T. Barclay [b], W. Cordes [b]

[a] *Department of Chemistry, IIT Kanpur, Kanpur 208016 U.P., India*
[b] *Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas, USA*

Received 5 December 1997

Abstract

A comparative study of the structural parameters of bis(dioxime) vitamin B_{12} models reveal an interesting squeezing of the metallabicycle. The lateral compression and the butterfly bending angle have a common origin in the steric bulk of the dioxime substituents. The first crystal structure of an organocobaloxime with cyclohexanedionedioxime(chgH) as the equatorial ligand is also reported. The compound $MeCo(chgH)_2Py$ crystallises in the monoclinic system, with the space group $P2_1/n$ with $Z = 4$ and unit cell parameters $a = 8.7074(9)$, $b = 9.3989(8)$, $c = 23.886(2)$ Å and $\beta = 91.862(8)°$.

Keywords: Bis(oxime)complexes; *Cis*-influences; Vitamin B_{12} model

---

1. Introduction

The extensive structural studies during the last three decades on cobaloximes[1], the well known vitamin B_{12} coenzyme model ([1]a–d) have been thoroughly compiled and meticulously reviewed [2]. As Co–C bond cleavage is the key step involved in the B_{12} or cobaloxime mediated reactions ([1]c–l), the change in the cobalt–carbon bond length as a function of steric and electronic factors with a wide range of the axial ligands in cobaloximes have been systematically investigated ([3]a). Among these, cobaloximes having bulky phosphines as the axial base ligand and 1-adamantyl cobaloxime represent in all probability the extreme limit to which the Co–C bond can be stretched ([3]a). Attempts have been made to achieve a quantitative rationalisation between structural, kinetic, equilibrium, spectroscopic, and thermodynamic properties of these complexes ([3]b–f).

Further, the unique structural features (a) the displacement of the cobalt atom from the mean N_4 plane {the d value}; (b) the upward or downward folding of the planar dioxH fragment, {the butterfly bending angle, α (Fig. 1)}; (c) the cobalt-axial base co-ordination; (d) twist of the plane of axial base with respect to the metallabicycle {the τ value (Fig. 1)}; (e) the O···O distance; and (f) the N···N distance {bite of the chelate ring}of these models have also been investigated ([2,3]g–j).

The structural studies on organocobaloximes with equatorial groups other than dmgH[2] have been few and are limited to a small number of gH [4], mpgH [5], and dpgH [6] complexes. In this paper we describe the hitherto un-noticed compression of the metallabicycle with increasing bulk of the dioxime substituent. Additionally, the first crystal structure of a cobaloxime with chgH as the equatorial ligand has been solved in order to view the picture in its totality.

---

* Corresponding author.

[1] Bis(dimethylglyoximato)cobalt (III).

[2] gH, glyoxime; dmgH, dimethylglyoxime; mpgH, methylphenylglyoxime; dpgH, diphenylglyoxime; chgH, cyclohexanedionedioxime.

0022-328X/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0022-328X(98)00462-8

2. Results and discussion

A careful study of the structural parameters of the five bis(dioxime) complexes (Table 1) point to some interesting observations on the squeezing of the metallabicycles with the increasing bulk of the dioximic substituents. Moving from gH to dpgH (see Fig. 1 for atom labelling scheme[3]) as the steric repulsions between the two substituent groups increase, the $C^{*}-C_{(ox)}$ bonds spread outwards, the $\angle C^{*}-C_{(ox)}-C_{(ox)}$ increases, the equatorial nitrogens come closer to each other {the N···N distance and the normalised bite (b)[4] decreases}, the $\angle N_{(1)}-Co-N_{(2)}$ and $\angle N_{(eq)}-C_{(ox)}-C_{(ox)}$ decreases, with a concomitant increase in the $\angle Co-N_{(eq)}-C_{(ox)}$ and $\angle N_{(1)}-Co-N'_{(1)}$

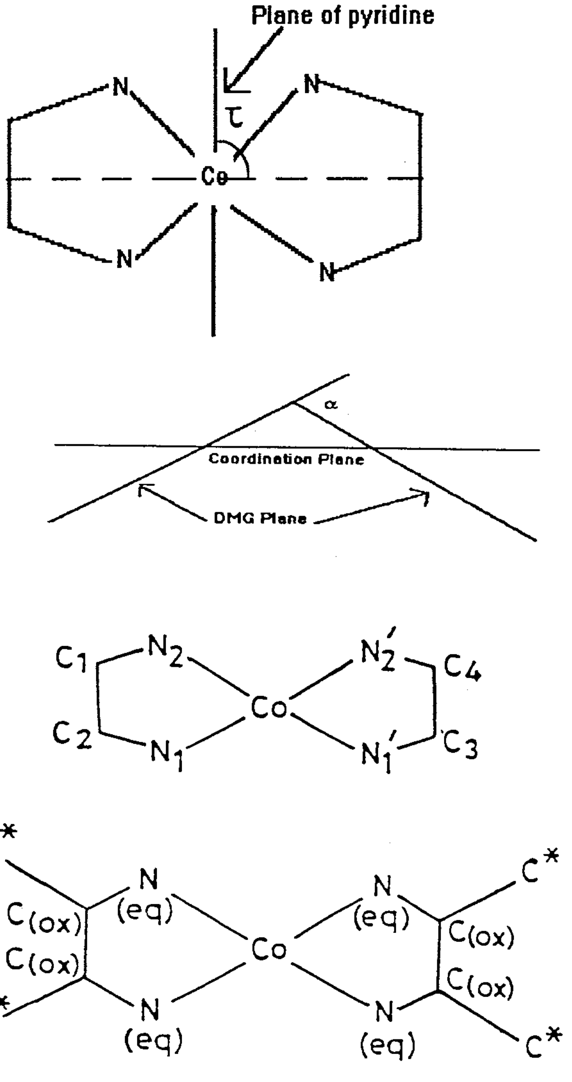
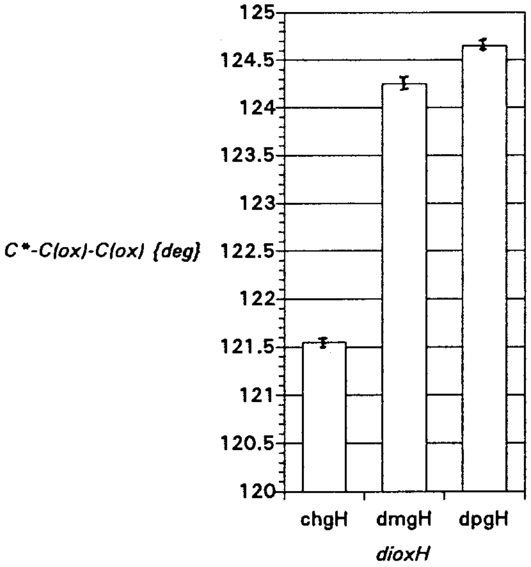
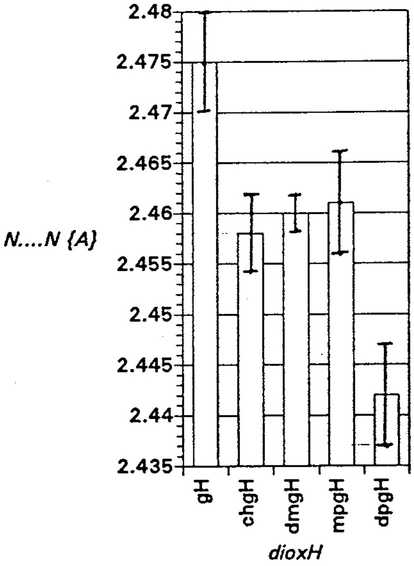
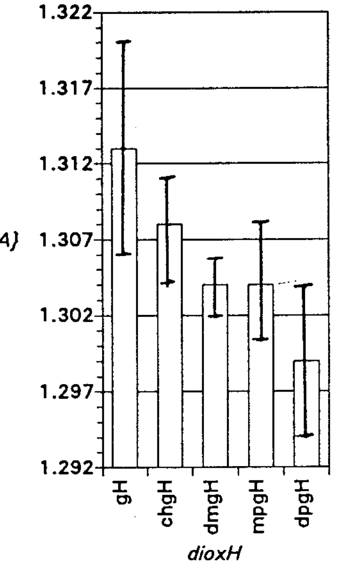


Fig. 1. Butterfly bending angle (α), the twist angle of pyridine (τ) and atom labelling scheme for the dioxime moiety.







---

[3] Both the labelling schemes have been used for convenience only.

[4] Normalised bite $\{/Co-N_{(eq)}\}$.

Table 1
Comparison of the structural parameters in bis(dioxime)RCo(dioxH)$_2$L[a] complexes

Parameter(dioxH)	gH ([4]b)	chgH (this study)	dmgH ([3]l), ([4]b)	mpgH [5][b]	dpgH ([6]a)
Co–C	2.005(4)	1.980(4)	1.998(5)	2.005(5)	1.997(4)
$Co–N_{(Py)}$	2.064(3)	2.057(3)	2.086(3)	2.094(4)	2.053(4)
$Co–N_{(eq)}$	1.884(3)	1.879(3)	1.897(4)	1.887(4)	1.883(2)
N=C	1.296(6)	1.291(5)	1.307(6)	1.300(6)	1.297(4)
N–O	1.338(5)	1.352(3)	1.352(6)	1.342(6)	1.342(6)
C–C	1.424(8)	1.470(6)	1.482(10)	1.462(7)	1.464(4)
$C–Co–N_{(Py)}$	178.0(2)	178.65(16)	178.0(2)	—	180.0
$C–Co–N_{(eq)}$	88.1–89.3	87.96(16)–88.65(16)	87.4–89.3	—	87.5–89.6
$N–Co–N_{(eq)}$	90.0–92.6	90.57(13)–92.5(1)	91.0–92.5	—	90.4(1)–92.73(12)
$Co–N_{(eq)}–O$	122.5–124.9	123.2(2)–124.2(2)	121.8–122.6	—	121.8(2)–122.0(2)
$Co–N_{(eq)}–C_{(ox)}$	114.4–116.0	116.3(3)–117.0(3)	116.3–117.8	—	117.4(2)
$N_{(eq)}–C_{(ox)}–C_{(ox)}$	113.1–114.3	112.2(3)–112.7 (4)	110.7–113.7	—	111.7(3)–112.5(3)
$C_{(ox)}–N_{(eq)}–O$	119.9–122.6	119.5(3)–120.0(3)	119.5–121.6	—	120.7(2)
$C^a–C_{(ox)}–C_{(ox)}$	—	121.55 (3)	124.25 (7)	—	124.65 (3)
$N_{(1)}–Co–N_{(2)}$	82.1 (1)[d]	81.69(14)	81.37(6)[d]	81.4(2)[d]	81.0(3)[d]
$N_{(1)}–Co–N'_{(1)}$	97.7(1)[d]	98.21(14)	98.60(6)[d]	98.0(1)[d]	98.9(3)[d]
O···O	2.49(1)[d]	2.498(4)	2.487(3)[d]	2.470(1)[d]	2.50(1)[d]
N···N	2.475(5)[d]	2.458(4)	2.460(2)[d]	2.461(5)[d]	2.442(5)[d]
α[e]	5.6[d]	3.23.2[d]	1.6[d]	0.0[d]	
d[f]	0.05[d]	0.0548(17)	0.04[d]	0.04[d]	0.05[d]
b[g]	1.313(7)[d]	1.308(4)	1.304(2)[d]	1.304(4)[d]	1.299(5)[d]
τ[h]	—	83.4	89.7	—	89.8[c,d]

[a] R, methyl unless otherwise stated; L, Py.

[b] R, CH_2CH_2CN.

[c] R, Et and L, 4-Me–Py.

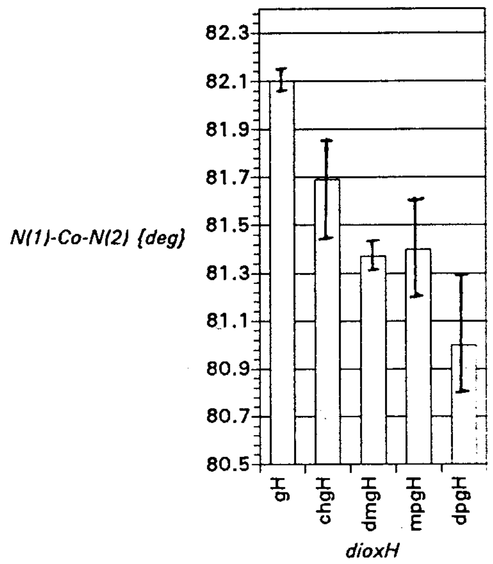
[d] Average values taken from ref. ([6]c).

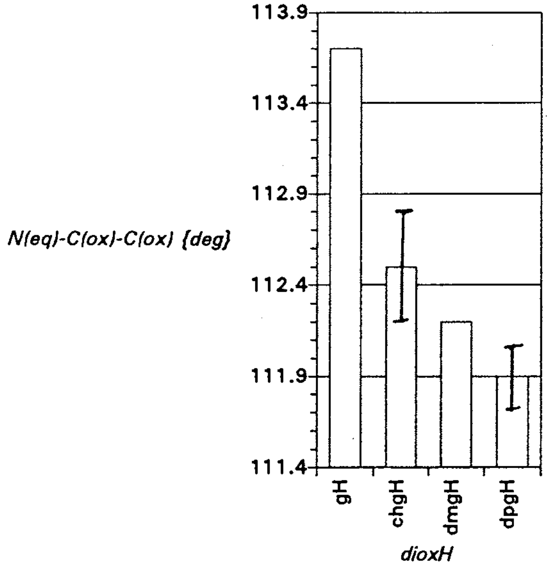
[d] Butterfly bending angle.

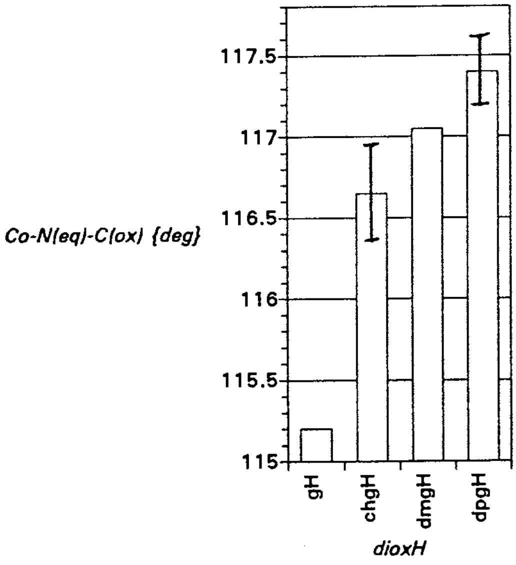
[e] The displacement of cobalt from the mean N_4 plane.

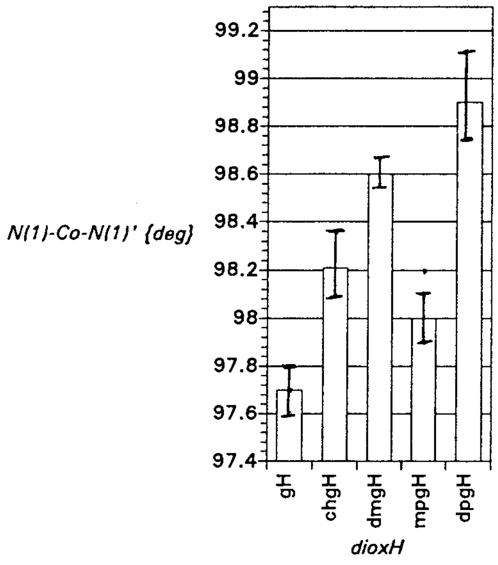
[f] Normalised bite {N···N/$Co–N_{(eq)}$}.

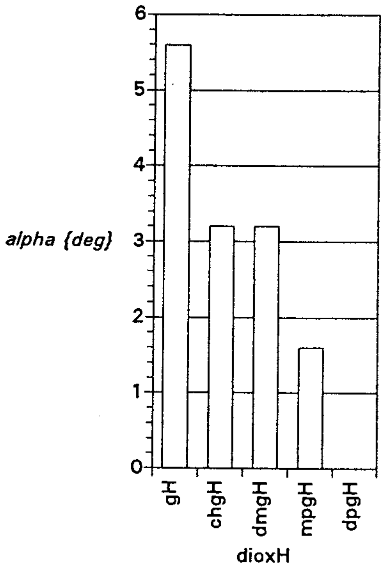
[h] Twist angle of pyridine wrt the line joining the midpoints of $C_2–C_3$ and $C_3–C_4$.











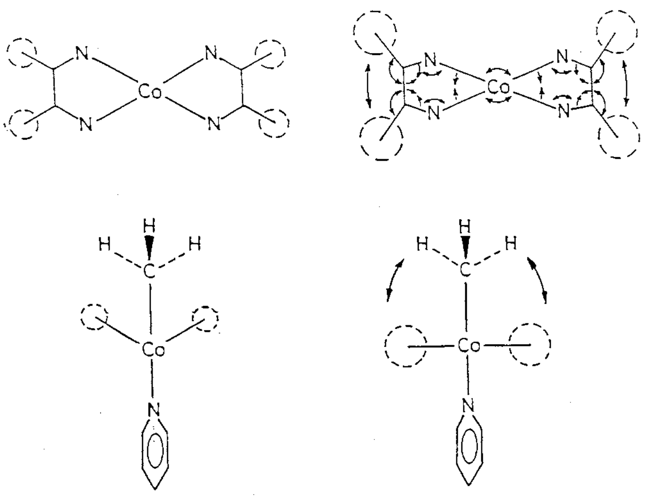


Fig. 2. Schematic representations of the lateral compression and the butterfly bending with the bulk of the dioxime substituents.

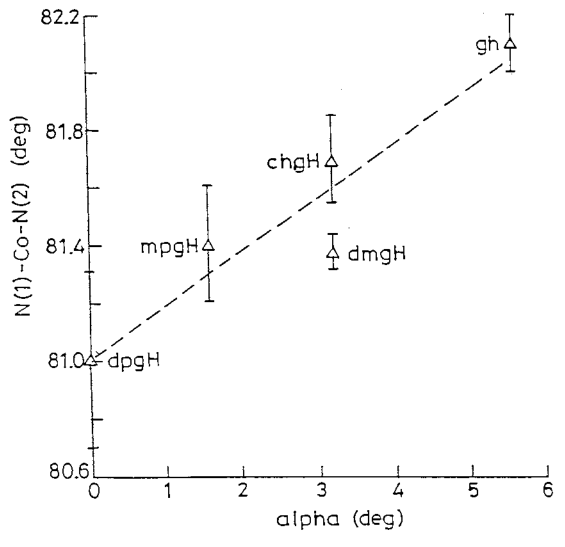


Fig. 3. Plot of $N_{(1)}$–Co–$N_{(2)}$ with alpha.

In effect, the two metallacycles are compressed perpendicular to the line joining the midpoints of C_1–C_2 and C_3–C_4 through cobalt (Fig. 2). In the chgH complex the C* atoms are held in place by the rest of the cyclohexane ring. Therefore, though the cyclohexane ring residues are bulkier than the four methyl groups, it is unable to compress the metallabicycle in comparison to the dmgH complex.

A comparison of the butterfly bending angles shows that as the bulk of the dioxime substituents increases the umbrella like fold of the two dioxime ligands towards the methyl group decreases i.e. they flatten out (steric *cis* influence) (Fig. 2)[5]. Apparently in all the complexes with substituted dioximes there is a increased

---

[5] Recently the interrelationship between the twist angle of the axial base and the butterfly bending angle has been established by Marzilli et al. ([3]j).

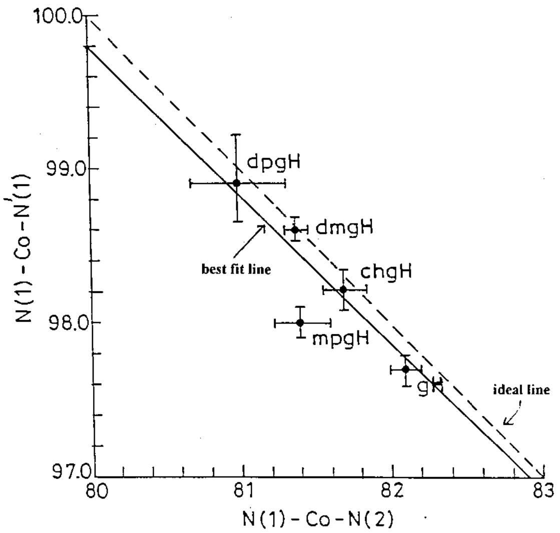


Fig. 4. Plot of $N_{(1)}$–Co–$N_{(2)}$ with $N_{(1)}$–Co–$N'_{(1)}$.

steric interaction with the axial methyl group as compared to the unsubstituted gH complexes where the interaction is with the hydrogens only. The chgH complex interestingly has the same butterfly bending angle as the dmgH. This indicates that the gross steric interactions of the dioxime substituents with the axial methyl group in dmgH and the chgH complexes are similar. The lateral compression and the butterfly bending angles are interrelated and have a common origin in the steric bulk of the dioxime substituents (see Fig. 3). Though the data points do not lie ideally on a straight line for a linear relationship, one can clearly see that as the steric bulk of the dioxime substituents increases, the α as well as $N_{(1)}$–Co–$N_{(2)}$ decreases.

A plot of the N_1–Co–N_2 vs. N_1–Co–N'_1 (Fig. 4), shows that the data for the chgH cobaloxime lies close to the line of ideal linear relationship between the two angles of the Co(dioxH)$_2$ moiety. This is similar to the behaviour of other cobaloximes with symmetrical ligands. The existence of a symmetry plane in the Co(dioxH)$_2$ (gH, dmgH, chgH, dpgH) which bisects the line joining the two O···O atoms is, in contrast, conspicuous by its absence in the analogous unsymmetrical mpgH complexes whose data lies much off the line ([6]c).

The ORTEP plot (30% thermal probability ellipsoid) of the structure of MeCo(chgH)$_2$Py [7] is shown in Fig. 5. Many hydrogens have been omitted for figure clarity. The cobalt atom is bound to the four nitrogen atoms of the two chgH ligands which forms a plane (all the nitrogen atoms being at a distance of ± 0.001(4) Å from the least square plane, see supplementary material). The cobalt atom itself deviates by 0.0548(17) Å {d value} out of the mean N_4 plane towards pyridine as in the analogous bis(dioxime) B_{12} models (Table 1).

The two dioxime ligands are bent towards the pyridine and are at an angle of 3.2° (the 'butterfly angle') with each other. The pyridine molecule maintains its planarity in the chgH complex, however its projection on the Co(dioxime) plane does not bisect the line joining the O···O atoms. This is in contrast to analogous bis(dioxime) complexes. The τ value of pyridine (83.4°) is surprisingly lower than any of the cobaloximes with pyridine as the axial base ligand ([6]c,[8]). The slight twist of the axial pyridine from the commonly observed value of 90° may be due to the unequal steric interactions between pyridine and the two cyclohexane ring residues having different conformations. Notice the disorder of the C_{91}/C_{92} and C_{101}/

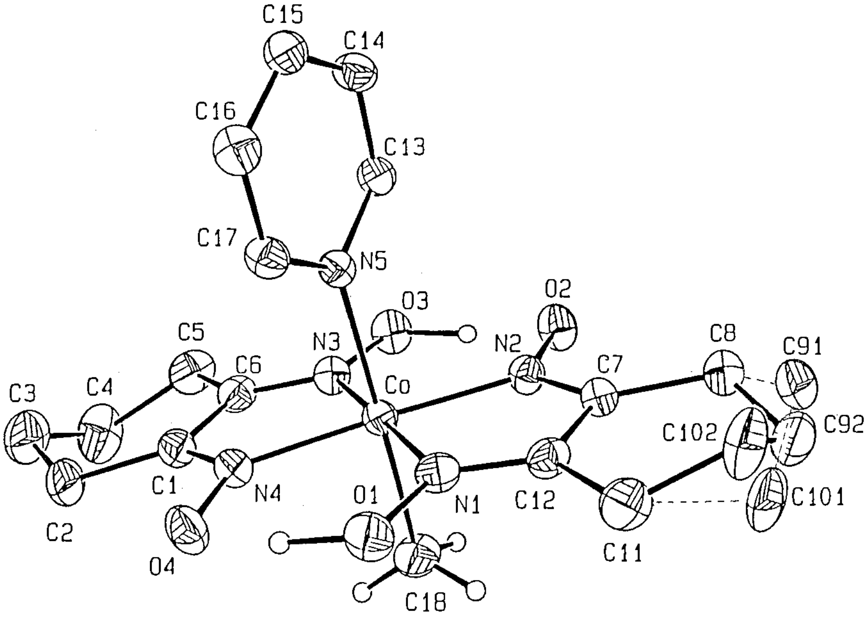


Fig. 5. ORTEP plot (30% thermal probability ellipsoid) of the structure of MeCo(chgH)$_2$Py (many hydrogens have been deleted for figure clarity).

C_{102} carbons on one of the 'wings' of the chgH complex.

The Co–C and the $N_{(Py)}$–Co bonds are perpendicular to the Co–$N_{(dioxime)}$ ones, and the $\angle$C–Co–$N_{(Py)}$ is linear as in other bis(dioxime) models. The Co–N, C=N, C–C and N–O distances are all in the range similar to the other bis(dioxime) complexes (see Table 1). The Co–C bond is not effected significantly with the change of the equatorial ligand, however among the five models compared, it is found to be the shortest in the chgH complex.

In the preceding discussion we have been able to establish that the upward folding of the metallabicycle towards the axial methyl group diminishes with increasing bulk of the dioxime substitutuent to minimise the steric interaction between the methyl group and the dioxime substituent (steric *cis* influence). This has a direct implication and relevance towards the understanding of the Co–C bond homolysis process in cobalamins as the postulated B_{12} cofactor localised mechanism for the Co–C bond cleavage includes, among other theories, the 'butterfly bending'[6] or the upward conformational theory ([2]b). In contrast, there is no evidence in literature to suggest the manifestation of the attendant lateral compression in cobalamins.

This is in all probability because, the existing data on cobalamins has not been previously examined in the way discussed above, and it is unlikely that the surrounding protein would expend energy to change the internal angles of the corrin ring. Besides, the crystal structures of only a few biologically occurring cobalamins have been solved ([9]b). To conclude, we foresee that the trends found above would add towards understanding of the organocobaloximes in particular and the cobalamins in general.

3. Experimental

The title compound, MeCo(chgH)$_2$Py [7] was synthesised and purified by column chromatography as reported earlier by us. Small orange crystals were grown in methanol by slow evaporation of the solvent and was subjected to X-ray diffraction analysis (Table 2). The disorder in one of the chgH ring was modelled with two sites for each of the ring atoms. The 60:40 occupancy ratio was established in early refinements with isotropic displacement parameters. These occupancy factors were then held fixed while all four partial atoms were allowed to refine with anisotropic displacement parameters. Selected bond angles and bond lengths are tabulated in Table 1 along the known data from the literature.

Table 2
Crystal, data collection and refinement parameters

Formula	$CoO_4N_5C_{18}H_{26}$
Fw	435.36
Crystal size (mm)	0.28 × 0.30 × 0.34
Cystal color	Orange
Crystal mount	On glass fiber with silcone glue
Unit cell dimensions	
a (Å)	8.7074(9)
b (Å)	9.3989(8)
c (Å)	23.886(2)
β (°)	91.862(8)
V (Å^3)	1953.8(3)
Cell detn, refls	25
Cell detn, 2θ range (°)	28–30
D_{calcd} (g cm^{-3})	1.48
Space group	$P2_1/n$
Z	4
F(000)	914
Radiation	Mo–K$_\alpha$ graphite Monochromated
λ (Å)	0.7107
Temperature (K)	293
Linear abs coeff (mm^{-1})	0.91
Diffractometer	Enraf-Nonius CAD-4
Scan technique	$\theta - 2\theta$
Scan width (°)	$1.0 + 0.35\tan\theta$
2θ range (°)	4–55
h,k,l ranges	−11, 11; −12, 0; 0, 31
STD reflection indices	0, −5, −11; 3, −5, 8; −3, 0, 15
Drift of STDs (%)	1.7
Absorption correction	Analytical
Absorption range	0.75–0.82
Refl measurements	4579
Unique refls	4477
R for merge	0.017
Data with $I > 1.0(I)$	3006
Solution method	Direct methods
Parameters refined	271
$R(F)$, $Rw(F)$	0.057, 0.055
GOF	1.37
p, $w-1 = [(2(I) + pI^2]/4F^2$	0.02
Largest Δ/σ	0.00
Final diff map (e Å^{-3})	−0.43(9), +0.42(9)
Programs	NRC386 (PC version of NRCVAX)[a]
Scattering factors	International tables for crystallography, vol. 4
H atom treatment	Idealized C–H = 0.95 Å

[a] [10].

The tables containing the final atomic co-ordinates, bond angles and bond lengths, thermal parameters, structure factors for all the atoms, and details of best planes have been deposited as supplementary materials.

---

[5] Butterfly bending angles are sensitive to lattice effects as studied by FT-Raman spectroscopy [9].

Acknowledgements

The work is supported by a grant from the DST, New Delhi. KQ is grateful to the Department of Atomic Energy, Bombay for the K.S. Krishnan Fellowship.

References

[1] (a)G.N. Schrauzer, Accounts Chem. Res. 1 (1968) 97. (b) K.L. Brown, in: D. Dolphin (Ed.) B_{12}, vol. 1, Wiley Interscience, New York, 1982, p. 245 and refs. cited therein. (c) J. Halpern, Science 227 (1985) 869. (d) R.G. Finke, D.A. Schiraldi, B.J. Mayer, Coord. Chem. Rev. 54 (1984) 1; for cobaloxime mediated free radical reactions. (e) L.I. Simandi, T.M. Barna, L. Koreeze, A. Rokenbauer, Tetrahedron Lett. 34 (1993) 317. (f) S. Nemeth, L. Simandi, J. Mol. Catal. 12 (1982) 87. (g) T.M. Brown, C.J. Cooksey, D. Crich, A.T. Dronsfield, R. Ellis, J. Chem. Soc. Perkin Trans. 1 (1993) 2131. (h) T.M. Brown, C.J. Cooksey, A.T. Dronsfield, A.S. Wilkinson, App. Organomet. Chem. 10 (1996) 415. (i) N.W Alcock, M.P. Atkins, B.T. Golding, P.J. Sellars, J. Chem. Soc. Dalton Trans. (1982) 337. (j) M.A. Ashcroft, M.P. Atkins, B.T. Golding, M.D. Johnson, P.J. Sellars, J. Chem. Res. (S) (1982) 216. (k) I. Das, S. Chowdhury, K. Ravikumar, S. Roy, B.D. Gupta, J. Organomet. Chem. 532 (1997) 101. (l) S. Roy, I. Das, K. Bhanuprakash, B.D. Gupta, Tetrahedron 50 (1994) 1847.

[2] (a) N. Bresciani-Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers, P.J. Toscano, Coord. Chem. Rev. 63 (1985) 1 and refs. cited therein. (b) L. Randaccio, N. Bresciani-Pahor, E. Zangrando, L.G. Marzilli, Chem. Soc. Rev. 18 (1989) 225.

[3] (a)N. Bresciani-Pahor, L. Randaccio, E. Zangrando, M.F. Summers, J.H. Ramsden, P.A. Marzilli, L.G. Marzilli, Organometallics 4 (1985) 2086. (b) L.G. Marzilli, F. Bayo, M.F. Summers, L.B. Thomas, E. Zangrando, N. Bresciani-Pahor, M. Mari, L. Randaccio, J. Am. Chem. Soc. 109 (1987) 6045. (c) K.L. Brown, S. Satyanarayana, J. Am. Chem. Soc. 114 (1992) 5674. (d) D. Datta, G.T. Sharma, J. Chem. Soc. Dalton Trans. (1989) 115. (e) N. Bresciani-Pahor, S. Germia, C. Lopez, L. Randaccio, E. Zangrando, Inorg. Chem. 29 (1990) 104. (f) R.S. Drago, J. Organomet. Chem. 512 (1996) 61. (g) L. Randaccio, S. Germia, E. Zangrando, C. Ebert, Inorg. Chem. 33 (1994) 4641. (h) J.P. Charland, E. Zangrando, N. Bresciani-Pahor, L. Randaccio, L.G Marzilli, Inorg. Chem. 32 (1993) 425. (i) S.M. Polson, R. Cini, C. Pifferi, L.G. Marzilli, Inorg. Chem. 36 (1997) 31. (j) S.M. Polson, L. Hansen, L.G. Marzilli, Inorg. Chem. 36 (1997) 307. (k) R.S. Drago, Inorg. Chem. 34 (1995) 3543. (l) A. Bigotto, E. Zangrando, L. Randaccio, J. Chem. Soc. Dalton (1976) 96.

[4] (a)P.J. Toscano, T.F. Swider, L.G. Marzilli, N. Bresciani-Pahor, L. Randaccio, Inorg. Chem. 22 (1983) 3416. (b) N. Bresciani-Pahor, L. Randaccio, E. Zangrando, P.J. Toscano, Inorg. Chim. Acta. 96 (1985) 193.

[5] A. Uchida, Y. Ohashi, Y. Sasada, Y. Ohgo, Acta Cryst. C41 (1985) 25.

[6] (a)C. Lopez, S. Alvarez, M. Font-Bardia, X. Solans, J. Organomet. Chem. 414 (1991) 245. (b) C. Lopez, S. Alvarez, M. Font-Bardia, X. Solans, IXth FECHEM Conference on Organometallic Chemistry, Heidelberg, Germany, 1991. (c) C. Lopez, S. Alvarez, X. Solans, M. Font-Bardia, Polyhedron 11 (1992) 1637. (d) J.M. Gilaberte, C. Lopez, S. Alvarez, M. Font-Bardia, X. Solans, New J. Chem. 17 (1993) 193.

[7] (a) G.N. Schrauzer, L.P. Lee, J.W. Sibert, J. Am. Chem. Soc. 92 (1970) 2997. (b) B.D. Gupta, K. Qanungo, J. Organomet. Chem. 543 (1997) 127.

[8] C. Lopez, S. Alvarez, X. Solans, M. Font-Altaba, Inorg. Chem. 25 (1986) 2962.

[9] (a)L. Randaciio, N. Bresciani-Pahor, J.D. Orbell, M. Calligaris, M.F. Summers, B. Snyder, P.J. Toscano, L.G. Marzilli, Organometallics 4 (1985) 469. (b) S. Nie, P.A. Marzilli, L.G. Marzilli, N.T. Yu, J. Am. Chem. Soc. 112, (1990) 6084.

[10] E.J. Gabe, Y. Lepage, J.P. Charland, F.L. Lee, P.S. White, NRCVAX, An Interactive Program System for Structure Ananlysis, J. Appl. Cryst. 22 (1989) 383.