B_{12} Models: Cobaloximes Containing Anisidine as Neutral Ligand

NEVENKA BRESCIANI-PAHOR, SILVANO GEREMIA, ENNIO ZANGRANDO*
Dipartimento di Scienze Chimiche, Universita' di Trieste, 34127 Trieste (Italy)
and ANDREA RAETO RASELLI
Laboratorium für Kristallographie, Universität Bern, CH-3012 Bern (Switzerland)

(Received November 16, 1988)

Abstract

The crystal and molecular structures of two vitamin B_{12} models containing anisidine as neutral ligand, anisidineCo(DH)$_2$alkyl, where (DH) = monoanion of dimethylglyoxime and alkyl = methyl (**1**), i-propyl (**2**) are reported. The compounds are isomorphous and crystallize in the space group $P\bar{1}$ with cell parameters $a = 8.556(2)$, $b = 11.038(2)$, $c = 12.035(2)$ Å, $\alpha = 104.63(2)$, $\beta = 91.59(1)$, $\gamma = 108.08(2)°$ for **1** and $a = 8.563(1)$, $b = 11.717(2)$, $c = 12.429(2)$ Å, $\alpha = 103.47(1)$, $\beta = 92.61(1)$, $\gamma = 108.71(2)°$ for **2**. The two structures were solved by conventional Patterson and Fourier methods and refined by least-squares methods to final R values of 0.038 (**1**) and 0.036 (**2**), using 3412 (**1**) and 3186 (**2**) independent reflections.

The axial N–Co–C fragment is characterized by Co–N and Co–C distances of 2.118(2) and 1.995(4) Å in **1** and 2.158(2) and 2.069(3) Å in **2**, respectively. Analysis of the Co–N bond lengths for complexes containing different N-donor ligands suggests that this distance is influenced by the basicity of the neutral ligand.

Introduction

Cobaloximes, molecules containing bis(dimethylglyoximato) as equatorial ligand, are the most extensively studied model system of vitamin B_{12} [1, 2]. Some quantitative relationships between structural, rate and NMR spectroscopic data have been previously reported [3, 4]. It has been found that the kinetic *trans* effect, expressed by $\log k_1$ for the displacement of the neutral ligand, linearly correlates with the Co–N(axial) bond distances. In fact, the plot of $\log k_1$ for 4CN–py versus Co–N(pyridine) bond lengths is fairly linear [1]. A similar relationship is also obtained when anisidine leaving rates are plotted against Co–N(aniline) distances, although less data are available [5]. Halpern *et al.* [6a] have shown that the Co–C bond dissociation energy (*BDE*)** linearly correlates with the pK_a of the neutral ligand in the series LCo(DH)$_2$CH(Me)Ph, where L are different 4-substituted pyridines. In order to have consistent structural and kinetic data and to assess the influence of the pK_a of the neutral ligand on the Co–N(axial) and Co–C bond distances, we report the structural characterization of two anisidineCo(DH)$_2$R complexes with R = Me (**1**), iPr (**2**).

Experimental

The two isomorphous compounds crystallize as orange–brown prisms. Unit cell parameters were determined from Weissenberg and precession photographs and refined on an Enraf-Nonius CAD4 single crystal diffractometer equipped with a graphite monochromator and Mo Kα radiation. The crystal parameters and the basic information on data collections and structure refinements are summarized in Table 1.

Three standard reflections measured every 4000 s showed no significant drift throughout the experiment for **1**. In the case of **2**, the intensities decreased by an average of 5.1% during the X-ray exposure time, and a linear correction to the data was applied. Intensities were corrected for Lorentz–polarization effects but not for absorption for both structures, because of the small crystal size and low μ values.

The structures were solved by Patterson and Fourier syntheses and full-matrix least-squares on F, with anisotropic temperature factors for non-hydrogen atoms, except C10A and C11A of **2** (see below). H atoms at calculated geometrical positions with isotropic $B = 1.3B_{eq}$ of the corresponding C atom in **1** and located on difference Fourier map with refined B values in **2**, were included as fixed contributors in the final least-squares cycles. Final R values are reported in Table 1. Enraf-Nonius SDP

---

*Author to whom correspondence should be addressed.

**For factors that influence the Co–C bond dissociation energy see ref. 6b.

0020-1693/89/$3.50

TABLE 1. Crystallographic data and refinement details for anisidineCo(DH)$_2$alkyl with alkyl = Me (**1**), iPr (**2**)

	1	**2**
Formula	$CoO_5N_5C_{16}H_{26}\cdot H_2O$	$CoO_5N_5C_{18}H_{30}\cdot H_2O$
Molecular weight	445.4	473.4
a (Å)	8.556(2)	8.563(1)
b (Å)	11.038(2)	11.717(2)
c (Å)	12.035(2)	12.429(2)
α (°)	104.63(2)	103.47(1)
β (°)	91.59(1)	92.61(1)
γ (°)	108.08(2)	108.71(2)
D_{calc} (g cm^{-1})	1.42	1.38
Z	2	2
Space group	$P\bar{1}$	$P\bar{1}$
μ (cm^{-1})	8.6	7.9
Crystal dimensions (cm^3)	0.03 × 0.03 × 0.04	0.025 × 0.04 × 0.03
No. reflections measured	5232	5451
No. independent reflections ($I > 3\sigma(I)$)	3412	3186
2ϑ max (°) (Mo Kα)	56	56
R	0.038	0.036
R_w	0.049	0.039
No. refined parameters	254	305
Weighting scheme	$1/(\sigma^2(F_o) + (0.02F_o)^2 + 1.0)$	$1/(\sigma^2(F_o) + 216 \times 10^{-6} \times F_o^2)$

programs [7] on a PDP 11/44 were used for **1**. For **2**, data reduction was performed with the SDP from Enraf-Nonius on a PDP 11/34 computer, solution and refinement of the structure were performed on an IBM-3033 computer using the SHELX76 program system [8]. Atomic scattering factors and anomalous dispersion correction terms (for non-H atoms) were those of ref. 9.

In **2** the i-Pr ligand was found to be disordered; the methyl carbon atoms C10, C11 and C10A, C11A (isotropically refined) present an occupancy factor of 0.81(1) and 0.19(1) respectively. The disorder may be interpreted assuming a rotation of about 70° of the i-Pr ligand around the Co—C9 bond.

Final positional parameters for non-hydrogen atoms are listed in Tables 2 and 3. See also 'Supplementary Material'.

Results and Discussion of the Structures

ORTEP drawings [11] of the molecules **1** and **2** with the atom numbering scheme are depicted in Figs. 1 and 2, respectively. The (DH)$_2$ ligand occupies the four equatorial positions of a distorted

TABLE 2. Atomic parameters of $MeOPhNH_2Co(DH)_2Me$ (**1**)

Atom	x/a	y/b	z/c	B_{eq} (Å^2)	Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Co	0.07933(4)	0.24862(3)	0.27422(3)	2.570(6)	C3	−0.0397(4)	0.1767(3)	0.4640(2)	3.48(6)
O1	−0.2654(3)	0.1876(2)	0.2144(2)	4.37(5)	C4	−0.0490(5)	0.1469(3)	0.5786(3)	5.32(8)
O2	0.2453(3)	0.2439(2)	0.4818(2)	4.27(5)	C5	0.5163(4)	0.3752(4)	0.1281(3)	5.08(9)
O3	0.4258(2)	0.3153(2)	0.3359(2)	4.04(5)	C6	0.3424(3)	0.3247(3)	0.1554(2)	3.31(6)
O4	−0.0869(3)	0.2512(2)	0.0677(2)	4.26(5)	C7	0.1948(4)	0.3049(3)	0.0784(2)	3.25(6)
O5	0.5145(3)	0.8361(2)	0.1718(2)	4.36(5)	C8	0.1989(5)	0.3246(4)	−0.0397(3)	4.93(8)
O6	0.2342(3)	0.5050(2)	0.6042(2)	4.59(5)	C9	0.0588(5)	0.0597(3)	0.2022(3)	4.48(7)
N1	−0.1461(3)	0.1940(2)	0.2941(2)	3.14(5)	C10	0.2012(3)	0.5499(2)	0.3037(2)	2.72(5)
N2	0.0978(3)	0.2202(2)	0.4209(2)	3.17(5)	C11	0.3683(3)	0.6102(3)	0.3463(2)	3.19(6)
N3	0.3042(3)	0.2982(2)	0.2521(2)	3.01(4)	C12	0.4688(4)	0.7050(3)	0.3003(2)	3.39(6)
N4	0.0596(3)	0.2696(2)	0.1250(2)	3.00(5)	C13	0.4035(3)	0.7407(3)	0.2111(2)	3.19(6)
N5	0.0968(3)	0.4483(2)	0.3503(2)	2.87(4)	C14	0.2391(4)	0.6795(3)	0.1666(2)	3.42(6)
C1	−0.3608(4)	0.1100(3)	0.4128(3)	5.00(8)	C15	0.1378(3)	0.5839(3)	0.2137(2)	3.33(6)
C2	−0.1858(4)	0.1607(3)	0.3879(2)	3.45(6)	C16	0.4478(5)	0.9037(3)	0.1061(3)	6.07(9)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = (4/3)\text{-}\Sigma_i\Sigma_j\beta_{ij}\,\mathbf{a}_i\,\mathbf{a}_j$.

TABLE 3. Atomic parameters of $MeOPhNH_2Co(DH)_2iPr$ (2)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq} (Å^2)	Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq} (Å^2)^a
Co	0.08120	0.26960	0.27400	3.863(7)	C5	0.5214(4)	0.4004(4)	0.1440(4)	6.75(8)
O1	−0.2664(2)	0.2032(2)	0.2080(2)	5.90(5)	C6	0.3483(3)	0.3514(3)	0.1672(3)	4.56(5)
O2	0.2441(2)	0.2744(2)	0.4811(2)	5.66(5)	C7	0.2011(4)	0.3316(3)	0.0894(2)	4.74(6)
O3	0.4282(2)	0.3422(2)	0.3432(2)	5.27(4)	C8	0.2083(6)	0.3575(4)	−0.0227(3)	7.14(9)
O4	−0.0824(3)	0.2750(2)	0.0721(2)	6.11(5)	C9	0.0720(4)	0.0890(3)	0.2029(3)	6.27(8)
O5	0.5159(3)	0.8318(2)	0.1757(2)	7.11(6)	C10	0.1768(9)	0.0434(5)	0.2642(5)	10.8(2)
O6	0.2280(3)	0.5096(2)	0.5971(2)	6.03(5)	C10A	0.183(4)	0.081(3)	0.115(2)	12.2(1)*
N1	−0.1464(3)	0.2138(2)	0.2883(2)	4.51(5)	C11	−0.0861(8)	0.0058(5)	0.1385(7)	14.3(3)
N2	0.0964(3)	0.2459(2)	0.4171(2)	4.48(4)	C11A	−0.055(3)	−0.003(2)	0.246(3)	9.1(8)*
N3	0.3079(3)	0.3244(2)	0.2592(2)	4.15(4)	C12	0.2012(3)	0.5571(2)	0.3019(2)	4.13(5)
N4	0.0637(3)	0.2927(2)	0.1307(2)	4.43(4)	C13	0.3679(3)	0.6197(3)	0.3465(3)	4.71(5)
N5	0.0987(3)	0.4604(2)	0.3455(2)	4.25(4)	C14	0.4679(4)	0.7102(3)	0.3027(3)	5.34(6)
C1	−0.3645(4)	0.1314(4)	0.3998(4)	6.65(9)	C15	0.4055(4)	0.7407(3)	0.2127(3)	4.94(6)
C2	−0.1878(4)	0.1832(3)	0.3784(3)	4.76(6)	C16	0.2413(4)	0.6780(3)	0.1664(3)	4.99(6)
C3	−0.0422(4)	0.2035(3)	0.4568(3)	4.94(6)	C17	0.1408(4)	0.5870(3)	0.2108(2)	4.72(6)
C4	−0.0497(6)	0.1778(5)	0.5688(3)	8.0(1)	C18	0.4564(6)	0.8774(4)	0.0929(4)	7.49(9)

^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{eq} = (8/3)\pi^2 \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$ (ref. 10).

octahedron around the Co atom. The four equatorial N atoms are coplanar within ±0.006(2) in **1** and ±0.002(2) Å in **2**, and the Co atom is displaced 0.033 Å in **1** and 0.003 Å in **2** from their mean plane towards anisidine. The two chemically equivalent halves of the equatorial moiety are approximately planar making a dihedral angle of 4.2(7) and 2.7(6)° in **1** and **2**, respectively, and bend towards the alkyl group.

In both crystals, in addition to the van der Waals forces, a water molecule of crystallization is involved in hydrogen bonding with the O2 and O3′ atoms of the unit at $-x$, $-y$, $-z$. The short contacts are 2.919(3), 2.915(3) Å in **1** and 2.847(3), 2.856(3) Å in **2**. The O···O distances of the oxime bridge vary from 2.461(3) to 2.487(3) Å, and fall within the mean values reported for cobaloximes [1].

The phenyl group of the anisidine ligand lies above one of the five-membered rings of the equatorial moiety, as already observed in aniline derivatives, $PhNH_2Co(DH)_2R$ [4]. The torsional angle MeO-C(Ph) is 18.5° in **1** and 7.6° in **2**, indicating that

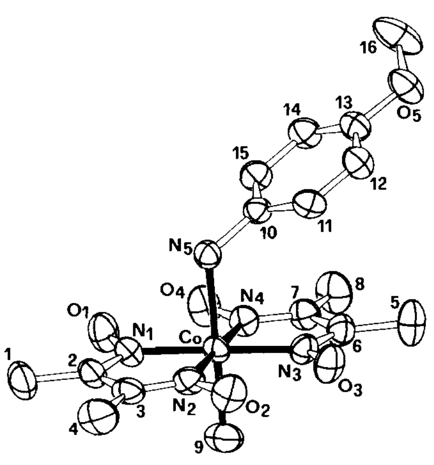

Fig. 1. ORTEP drawing (thermal ellipsoid; 50% probability) and labeling scheme for non-H atoms of **1**. The C atoms are labeled by their ordering number in the coordinate list.

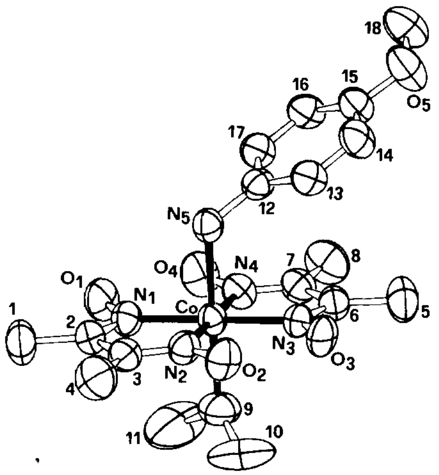

Fig. 2. ORTEP drawing (thermal ellipsoid; 50% probability) and labeling scheme for non-H atoms of **2**. Only the iPr group in the highest occupancy factor (see text) is depicted.

TABLE 4. Comparison of axial bond lengths in some $LCo(DH)_2R$ complexes and pK_a values of L

L/R	Co–N (Å)	Co–C (Å)	pK_a	Reference
anisidine/Me	2.118(2)	1.995(4)	5.34	this work
aniline	2.129(1)	1.992(2)	4.63	5
anisidine/iPr	2.158(2)	2.069(3)	5.34	this work
aniline	2.177(2)	2.068(3)	4.63	5
py/CH(Me)COOMe	2.058(7)	2.083(7)	5.22	13
4Cl-py	2.06(1)	2.07(2)^a	3.85	14
4CN-py	2.076(6)	2.098(7)	1.90	15
4Me-py/CH(Me)CN	2.058(8)	2.05(1)	6.00	16
py	2.047(3)	2.053(4)	5.22	17
4CN-py	2.065(3)	2.052(6)	1.90	18

^{a}Mean value.

the carbon atom of the methoxy group lies nearly in the plane of the phenyl ring, as usually found in compounds containing the methoxyphenyl group, possibly in order to permit a better conjugation [12]. The Co–N–Ph bond angle is 118.5(2)° in **1** and 119.4(2)° in **2**. The axial fragment in **1** is characterized by Co–C and Co–N distances and N–Co–C angle of 1.995(4), 2.118(2) Å and 179.1(1)°, respectively. The corresponding values in **2** are 2.069(3), 2.158(2) Å and 178.0(1)°.

Relevant geometric parameters for some $LCo(DH)_2R$ complexes are reported in Table 4. The Co–N axial bond length varies significantly with the increasing σ-donor power of the alkyl group in the order Me < iPr (electronic *trans* influence) [1]. For the same alkyl group, the Co–N bond length in anisidine complexes is slightly but significantly shorter than that of the aniline analogs. For $MeCo(DH)_2L$, this shortening parallels the decrease of $\log k_1$ for the displacement of the neutral ligand from 0.18 (L = aniline) to −0.33 (L = anisidine) [19]. The Co–N bond length seems to decrease as the pK_a of the neutral ligand increases. An analogous trend is observed for 4-X-py derivatives with R = CH(Me)COOMe and CH(Me)CN (Table 4). Although these data are less accurate, it seems that the shortening of the Co–N distance with the increase of pK_a is less enhanced in the four-substituted pyridine derivatives. A quantitative relationship of the dependence of the Co–N bond length on the pK_a of the base is difficult to assess from the present data. We tentatively suggest that the Co–N distance should be more influenced by a perturbation, such as a different neutral ligand basicity, when the Co–N bond is longer (i.e. weaker) as in aniline derivatives [4, 20] than when it is shorter (i.e. stronger), as in pyridine compounds.

For the same alkyl group, the Co–C bond length is essentially unaffected by the change of the neutral ligand containing either N-sp^2 or N-sp^3 donors. On the other hand, Halpern *et al.* [6] reported a linear relationship between the pK_a of the base and the bond dissociation energy (**BDE**) of the Co–C distances in the series $LCo(DH)_2CH(Me)Ph$ with L = $4NH_2py$, 4Mepy, py, 4CNpy, suggesting that the Co–C bond is labilized by a more acid neutral ligand. No structural information is available for the CH(Me)Ph derivatives, but for those with R = CH(Me)CN and CH(Me)COOMe reported in Table 4, no significant difference is detected in Co–C distances.

Supplementary Material

Anisotropic thermal parameters, hydrogen atom coordinates, bond lengths and angles and tables of observed and calculated structure factors are available from the authors on request.

Acknowledgements

This work was supported by grants from MPI and CNR (Rome). The authors are indebted to Prof. L. G. Marzilli (Atlanta, U.S.A.) for supplying the crystals.

References

1 N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev., 63* (1985) 1.
2 L. Randaccio, N. Bresciani-Pahor, E. Zangrando and L. G. Marzilli, *Chem. Soc. Rev., 16* (1989) 229.
3 E. Zangrando, N. Bresciani-Pahor, L. Randaccio, J. P. Charland and L. G. Marzilli, *Organometallics, 5* (1986) 1938.
4 L. G. Marzilli, F. Bayo, M. F. Summers, L. B. Thomas, E. Zangrando, N. Bresciani-Pahor, M. Mari and L. Randaccio, *J. Am. Chem. Soc., 109* (1987) 6045.
5 M. Mari, *Thesis*, University of Trieste, 1985.

6 (a) F. T. T. Ng, G. L. Rempel and J. Halpern, *J. Am. Chem. Soc., 104* (1982) 621; (b) J. Halpern, *Science, 227* (1985) 869.

7 B. A. Frenz, *Structure Determination Package,* Texas A&M University, College Station, TX, U.S.A. and Enraf-Nonius, Delft, The Netherlands, 1983.

8 G. M. Sheldrick, *SHELX76,* program for crystal structure determination, University of Cambridge, Cambridge, U.K., 1976.

9 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1979. (Present distributor D. Reidel, Dordrecht.)

10 V. Schomaker and R. E. Marsh, *Acta Crystallogr., Sect. A, 39* (1983) 819.

11 C. K. Johnson, *ORTEP, Report ORNL 3794,* Oak Ridge, National Laboratory, TN, U.S.A., 1965.

12 W. Hummel, K. Huml and H. B. Bürgi, *Helv. Chim. Acta, 71* (1988) 1291.

13 T. Kurihara, Y. Ohashi and Y. Sasada, *Acta Crystallogr., Sect. B, 38* (1982) 2484.

14 T. Kurihara, Y. Ohashi, Y. Sasada and Y. Ohgo, *Acta Crystallogr., Sect. B, 39* (1983) 243.

15 T. Kurihara, A. Uchida, Y. Ohashi, Y. Sasada and Y. Ohgo, *Acta Crystallogr., Sect. C, 40* (1984) 1557.

16 A. Uchida, Y. Ohashi, Y. Sasada, Y. Ohgo and S. Baba, *Acta Crystallogr., Sect. B, 40* (1984) 473.

17 Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada and Y. Ohgo, *J. Am. Chem. Soc., 104* (1982) 6353.

18 Y. Ohashi, A. Uchida, Y. Sasada and Y. Ohgo, *Acta Crystallogr., Sect. B, 39* (1983) 54.

19 Q. Chen, L. G. Marzilli, N. Bresciani-Pahor, L. Randaccio and E. Zangrando, *Inorg. Chim. Acta, 144* (1988) 241.

20 W. O. Parker, Jr., E. Zangrando, N. Bresciani-Pahor, L. Randaccio and L. G. Marzilli, *Inorg. Chem., 25* (1986) 3489.