Inorganica Chimica Acta, *96* (1985) 193–198

Organocobalt B_{12} Models.
Structures of *trans*-Bis(glyoximato)(alkyl)(pyridine)cobalt(III), with Alkyl = Me, Et, i-Pr

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Received April 16, 1984

Abstract

The crystal structures of the organocobalt complexes, $pyCo(GH)_2Me$(1), $pyCo(GH)_2Et$(2) and $pyCo(GH)_2Pr^i$(3) (py = pyridine, GH = monoanion of glyoxime) are reported. Compound (**1**) crystallizes in the space group $P2_12_12_1$ with cell parameters a = 8.508(1), b = 13.586(2) and c = 11.614(6) Å; (**2**) crystallizes in the space group $P2_12_12_1$ with cell parameters a = 8.448(4), b = 12.164(2) and c = 13.651(2) Å; (**3**) crystallizes in the space group $P2_1/c$ with cell parameters a = 8.443(7), b = 12.913(2), c = 14.341(2) Å and β = 92.86(4).

The three structures have been solved by Patterson and Fourier methods and refined by least squares methods to final R values of 0.045(**1**), 0.068(**2**) and 0.057(**3**) using 1819(**1**), 1653(**2**) and 1582(**3**) independent reflections. The py–Co–alkyl fragment shows significant variation of Co–N and Co–C bond lengths. The latter increase from 2.003(4) to 2.084(9) Å following the increase of the alkyl bulk. The Co–N(py) distances increase from 2.064(3) to 2.101(6) Å with the increasing σ-donor power of the alkyl group *trans* to pyridine. In comparison with cobaloximes having the same axial ligands, $pyCo(DH)_2$-alkyl (DH = monoanion of dimethylglyoxime) does not show significant differences on the py–Co–alkyl fragment. Co–N axial bond lengths and exchange rates of the axial neutral ligand are consistent for the two series, although changes in bond lengths are detected only when rate constants are from two to three orders of magnitude different.

Introduction

Previous studies on vitamin B_{12} models, namely octahedral LCo(chel)alkyl complexes, have recently shown [1] that dramatic changes in the ligand exchange rates occur when chel is changed from bis(dimethylglyoximato)($(DH)_2$) to bis(salicylaldehyde)-*o*-phenylendiiminato, (saloph) dianion. The ligand exchange rates of the saloph derivatives for the reaction (1) have been estimated to be about 10 times larger than those of the analogous cobaloximes having the same axial ligands. This enormous *cis*-influence was partly attributed to a ground state effect and partly to the stability of pentacoordinate Cosaloph derivatives, higher than that of cobaloximes [1]. Similar evidences have been reported by Brown and Milton [2], who have shown that Co(acacen) (acacen = dianion of N,N(acetylacetone)-ethylendiamine) system is very reactive

$$\text{LCo(chel)alkyl} + \text{L}' \longrightarrow \text{L}'\text{Co(chel)alkyl} + \text{L} \qquad (1)$$

followed by Co–corrin and cobaloxime systems.

Therefore, the value of the Co–L bond length should partly reflect the effects of the chel ligand change. In fact, the Co–N(py) bond in the series pyCo(saloph)alkyl is about 0.1 Å longer than the Co–N(py) bond in the series $pyCo(DH)_2alkyl$ (alkyl = Et, CH_2CF_3, CH_2NO_2, CH_2CN) [1, 3].

Less dramatic changes in reactivity have been reported when the DH ligand is substituted by the glyoximato ligand, GH. Thus, the $LCo(DH)_2alkyl$ complexes undergo ligand exchange of the neutral axial ligand at rates up to 100 times faster than those of the corresponding $LCo(GH)_2$ alkyl analogues [4]. The differences in reactivity between the two series when L = PR_3 and alkyl = Me (R = OMe, Ph, c-C_6H_{11}) were found to correspond to very small changes in the axial Co–P distances [4]. Therefore, it was of interest to determine the molecular structure of the series $pyCo(GH)_2$ alkyl (alkyl = Me (*1*), Et (*2*), i-Pr (*3*)) for a further comparison of their structural and rate values with those of the corresponding cobaloximes already structurally characterized [5–7].

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TABLE I. Crystallographic Data for (*1*), (*2*) and (*3*).

Formula	$CoO_4N_5C_{10}H_{14}$	$CoO_4N_5C_{11}H_{16}$	$CoO_4N_5C_{12}H_{18}$
M	327.23	341.26	355.28
a	8.508(1)	8.448(4)	8.443(7)
b	13.586(2)	12.164(2)	12.913(2)
c	11.614(6)	13.651(2)	14.341(2)
β (°)			92.86(4)
D_c (g cm^{-3})	1.62	1.62	1.51
D_m	1.63	1.61	1.52
Z	4	4	4
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
μ(MoKα) cm^{-1}	12.9	12.4	11.2
Crystal dimensions (cm^3)	0.03 x 0.03 x 0.01	0.04 x 0.04 x 0.01	0.03 x 0.02 x 0.01
No. Collected reflections	2246	2343	4892
No. Independent reflections	1819	1653	1582
θ max (°)	30°	30°	30°
R	0.045	0.068	0.057
R_w	0.056	0.083	0.064

Experimental

Crystal Data

The crystals were obtained as described in ref. 4. The cell parameters were determined and refined on a CAD4 single crystal diffractometer. The crystal data are given in Table I. Intensities of three check reflections were measured during the data collection about every 100 reflections, and did not show any systematic variation throughout the data recording. Intensities having $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors. Anomalous dispersion correction was applied. Empirical absorption correction did not affect the final *R* indexes and therefore was not included.

Solution and Refinement of the Structures

All the three structures were solved by conventional Patterson and Fourier methods and refined by full-matrix diagonal least-squares methods. The final cycles were carried out including the contribution, held constant (B = 5 Å^2), of hydrogen atoms at calculated positions and the anisotropic temperature factors for all the non-hydrogen atoms.

The final *R* and R_w values are given in Table I. The final weighting scheme was: $1/(\sigma^2(F) + (p\cdot F)^2 + q)$, where p = 0.02 and q = 1 for all the three structures [8]. Atomic scattering factors were those given in ref. 9. All the calculations were carried out by using the SPD-CAD4 programs on a PDP11-44 computer. Final positional parameters of non-hydrogen atoms and their *B*eq (Å^2) are given in Table II. Hydrogen atom coordinates, anisotropic thermal parameters, calculated and observed structure factors are available from the Editor.

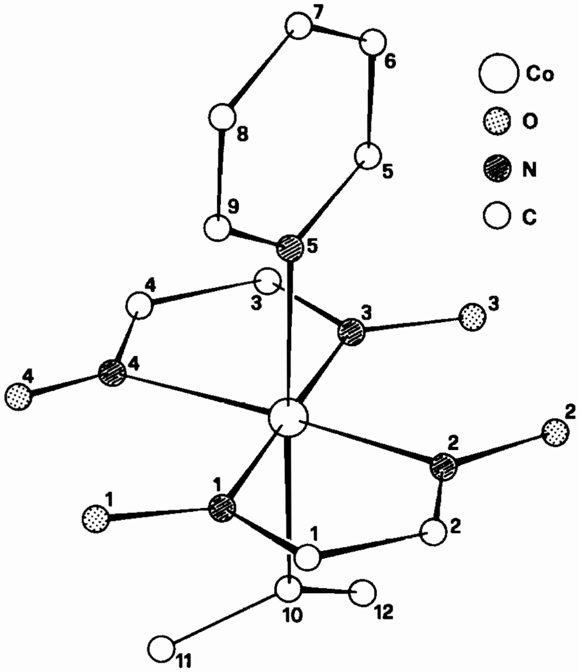

Fig. 1. Numbering scheme for the atoms of the crystallographically independent molecule of (3). The same scheme applies to (1) excluding C(11) and C(12) and to (2) excluding C(12).

Results and Discussion

The non-hydrogen atom numbering scheme for the crystallographically-independent molecule of (3) is given in Fig. 1, and it also applies to the crystallographically-independent molecules of (1) and (2).

TABLE II. Table of Positional Parameters and their Estimated Standard Deviations.[a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Compound (*1*)				
Co	0.03182(7)	0.01594(4)	0.13743(5)	2.382(8)
O1	0.3404(4)	−0.0381(3)	0.2096(4)	4.77(9)
O2	−0.0548(5)	0.1661(3)	−0.0254(4)	4.48(8)
O3	−0.2752(4)	0.0779(3)	0.0721(4)	4.17(8)
O4	0.1174(5)	−0.1284(3)	0.3010(3)	4.81(9)
N1	0.2540(4)	0.0213(3)	0.1417(4)	3.62(8)
N2	0.0613(5)	0.1191(3)	0.0303(4)	3.22(8)
N3	−0.1899(4)	0.0174(3)	0.1369(4)	3.01(6)
N4	0.0001(5)	−0.0815(3)	0.2483(4)	3.11(7)
N5	0.0354(5)	−0.0903(3)	0.0104(3)	2.50(6)
C1	0.3167(6)	0.0867(5)	0.0747(5)	4.4(1)
C2	0.2064(7)	0.1437(4)	0.0119(5)	4.1(1)
C3	−0.2542(6)	−0.0462(4)	0.2058(5)	3.6(1)
C4	−0.1444(7)	−0.1034(4)	0.2705(5)	3.9(1)
C5	−0.0541(7)	−0.0833(4)	−0.0826(5)	4.1(1)
C6	−0.0626(7)	−0.1534(4)	−0.1670(4)	3.9(1)
C7	0.0261(7)	−0.2366(4)	−0.1572(5)	4.0(1)
C8	0.1198(9)	−0.2454(5)	−0.0606(6)	6.4(1)
C9	0.1213(7)	−0.1715(4)	0.0193(5)	5.0(1)
C10	0.0258(7)	0.1156(4)	0.2647(5)	4.0(1)
Compound (*2*)				
Co	0.2107(1)	0.15317(8)	0.27651(7)	2.06(1)
O1	0.1239(8)	−0.0091(5)	0.1382(5)	4.1(1)
O2	0.5189(7)	0.2141(6)	0.3389(6)	4.1(1)
O3	0.2986(9)	0.3130(5)	0.4202(5)	4.1(1)
O4	−0.1006(7)	0.0846(6)	0.2215(6)	4.3(1)
N1	0.2412(7)	0.0430(5)	0.1830(5)	2.6(1)
N2	0.4346(7)	0.1500(6)	0.2795(5)	2.7(1)
N3	0.1791(8)	0.2605(6)	0.3729(5)	2.8(1)
N4	−0.0143(7)	0.1506(7)	0.2793(6)	3.2(1)
N5	0.2110(8)	0.2693(5)	0.1660(5)	2.3(1)
C1	0.390(1)	0.0206(7)	0.1628(7)	3.2(2)
C2	0.4996(9)	0.0834(7)	0.2192(7)	3.2(2)
C3	0.032(1)	0.2806(8)	0.3960(7)	3.6(2)
C4	−0.078(1)	0.2166(9)	0.3401(7)	3.6(2)
C5	0.295(1)	0.3615(8)	0.1718(7)	4.4(2)
C6	0.302(2)	0.4384(8)	0.0977(7)	4.8(2)
C7	0.226(1)	0.4193(8)	0.0124(7)	4.2(2)
C8	0.138(2)	0.3227(9)	0.0046(7)	4.7(2)
C9	0.135(1)	0.2520(8)	0.0807(8)	3.9(2)
C10	0.211(1)	0.0430(8)	0.3873(6)	3.6(2)
C11	0.221(2)	−0.075(1)	0.3659(9)	6.3(3)
Compound (*3*)				
Co	0.2695(1)	0.05684(7)	0.27568(7)	3.11(2)
O1	0.1986(7)	−0.1178(4)	0.3878(4)	6.0(1)
O2	0.5733(6)	0.1337(4)	0.2280(4)	5.4(1)
O3	0.3363(6)	0.2320(4)	0.1644(4)	5.7(1)
O4	−0.0339(6)	−0.0219(5)	0.3190(4)	6.3(1)
N1	0.3118(7)	−0.0581(5)	0.3532(4)	4.1(1)
N2	0.4933(6)	0.0624(5)	0.2771(4)	3.9(1)
N3	0.2264(7)	0.1744(5)	0.2022(4)	4.0(1)
N4	0.0468(6)	0.0523(5)	0.2770(4)	4.0(1)
N5	0.2671(7)	−0.0377(5)	0.1564(4)	4.2(1)

(continued overleaf)

TABLE II. *(continued)*

Atom	x	y	z	B (A$_2$)
C1	0.4619(9)	−0.0778(6)	0.3698(6)	4.7(2)
C2	0.5652(8)	−0.0086(7)	0.3242(6)	4.6(2)
C3	0.076(1)	0.1935(6)	0.1844(6)	5.2(2)
C4	−0.0258(9)	0.1233(7)	0.2298(7)	5.4(2)
C5	0.298(1)	−0.0026(8)	0.0740(6)	7.7(3)
C6	0.298(2)	−0.0599(9)	−0.0059(7)	10.2(4)
C7	0.267(1)	−0.1593(8)	−0.0029(7)	7.6(3)
C8	0.242(1)	−0.2026(7)	0.0790(8)	8.8(3)
C9	0.239(1)	−0.1381(7)	0.1579(7)	7.7(3)
C10	0.281(1)	0.1480(7)	0.3957(6)	5.7(2)
C11	0.164(1)	0.122(1)	0.4660(7)	8.2(3)
C12	0.296(2)	0.2603(9)	0.3829(9)	10.5(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

TABLE III. Comparison of the Geometry of PyCo(chel)alkyl Complexes Having chel = $(GH)_2$ and $(DH)_2$. Mean values of bond lengths (Å) with their mean e.s.d.s in parentheses and the ranges of the bond angles (°) are given. The geometry of glyoxime GH_2 and dimethylglyoxime DH_2 is also reported.

Alkyl	Me		Et		Pr^i		Gh$_2$[d]	DH$_2$[e]
	GH	DH[a]	GH	DH[b]	GH	DH[c]		
Co–C	2.005(4)	1.998(5)	2.020(7)	2.035(5)	2.084(9)	2.085(3)		
Co–N	2.064(3)	2.068(3)	2.067(6)	2.081(3)	2.101(6)	2.099(2)		
Co–Neq	1.884(3)	1.897(4)	1.883(6)	1.884(4)	1.881(6)	1.887(2)		
N–C	1.296(6)	1.307(6)	1.292(10)	1.295(6)	1.290(9)	1.308(4)	1.2849(8)	1.288(3)
N–O	1.338(5)	1.352(6)	1.339(8)	1.363(5)	1.340(7)	1.348(3)	1.3854(8)	1.410(3)
C–C	1.424(8)	1.482(10)	1.431(12)	1.473(7)	1.429(11)	1.458(4)	1.453(1)	1.474(3)
N–Co–C	178.0(2)	178.0(2)	178.4(3)	177.1(2)	177.5(3)	175.4(1)		
Neq–Co–C	88.1–89.3	87.4–89.3	86.4–92.0	85.9–93.0	87.5–90.9	86.4–92.2		
Neq–Co–N	90.0–92.6	91.0–92.5	89.5–92.1	89.3–93.1	90.0–91.2	89.9–91.4		
Co–Neq–O	122.5–124.9	121.8–122.6	122.4–123.8	121.6–123.2	122.9–124.4	122.3–123.0		
Co–Neq–C	114.4–116.0	116.3–117.8	115.1–115.9	117.2–117.5	114.6–115.3	116.4–117.4		
C–Neq–O	119.9–122.6	119.5–121.6	120.3–122.2	119.2–121.0	120.4–121.8	119.5–121.2	118.00(5)	113.2(1)
N–Ceq–C	113.1–114.3	110.7–113.7	112.7–114.6	110.8–112.9	113.1–114.4	111.9–112.8	112.31(5)	114.1(1)
Co–C–C			119.9(7)	117.8(4)	116.2(8)	114.2(2)		
d (Å)	0.05	0.04	0.04	0.05	0.03	0.02		
α (°)	5.6	6.3	1.1	9.1	1.9	4.2		

[a] Ref. [5]. [b] Ref. [7]. The neutral ligand is 4-(HN=C(OMe))py. [c] Ref. [6]. [d] Ref. [10]. [e] Ref. [11].

In all the three complexes the cobalt has a distorted octahedral geometry, with the GH ligands occupying the equatorial positions. Relevant bond lengths and angles are reported in Table III together with the corresponding values for the analogous (DH) complexes and for the free ligands. The displacement, d, of Co out of the 4-N equatorial coordination plane toward pyridine and the bending angle, α, between the planes passing through the two GH moieties are also given in Table III.

Previous comparison of the structure of some GH and DH complexes having the same set of axial ligands, namely MeCo(chel)PR_3 (R = Ph, MeO) did not show any significant difference in the comparable bond lengths and angles of the Co(chel) moiety. Inspection of Table III, however, suggests that small differences may be detected in the C–C and N–O distances and in the angles involving these bonds, which are shorter in the GH complexes, although thermal motion of N, C and O atoms could influence these values. A similar trend is observed in the free ligands.

As expected, the Co–C bond length increases from 2.005(4) Å to 2.084(9) Å with the increasing bulk of

TABLE IV. Comparison of Co–N(py) Bond Lengths and of Rate Constants for the Ligand Exchange Reaction pyCo(chel)alkyl + $PBu_3^n \rightarrow PBu_3^n$Co(chel)alkyl + py where chel = $(GH)_2$ or $(DH)_2$.

alkyl	Co–N(py) (Å)		Kobs (s^{-1})^a	
	GH	DH	GH	DH
Me	2.064(3)	2.068(3)	8.7×10^{-5}	8.0×10^{-3}
Et	2.067(6)	2.081(3)^b	3.0×10^{-3}	8.7×10^{-2}
Pr^i	2.101(6)	2.099(2)	5.2×10^{-2}	3.0

^{a}Ref. [4]. ^{b}See note *b* of Table III.

the alkyl group [12]. These values are equal to those reported for the $(DH)_2$ derivatives, within experimental error. Analogously, the Co–N(py) distance increases from 2.064(3) to 2.101(6) with the increasing σ-donor power of the *trans* alkyl group and parallels the trend already observed for cobaloximes containing the same alkyl groups [12].

Both Co–N(py) distances and Kobs (Table IV) increase along the series with the same equatorial ligand when the axial ligand varies from Me to Pr^i, and follow the increasing σ-donor power of the axial alkyl group. In both GH and DH series the Kobs (Pr^i)/Kobs(Me) is larger than one thousand.

The results show that the change of the equatorial ligand from DH to GH does not affect the axial bond lengths. Consequently, the peripheral methyl groups of the equatorial DH ligands do not interact significatly with axial ligands such as pyridine or the above alkyl groups. However, rate constants for ligand exchange, Table IV, NMR data at the reaction of the correlated $P(OMe)_3$ have been interpreted to suggest that GH is a poorer electron-donor than DH (*4*). In fact the rate constants for the DH series are larger (from 10 to 100 times) than those of the GH series. Therefore it may be concluded that both kinetic and structural results are consistent, although changes in bond lengths due to different equatorial ligands may be reliably detected only when variations in rate constants are from two to three orders of magnitude. This conclusion is also in agreement with previous results [1] derived from the comparison of $LCo(DH)_2CH_2CN$ and $LCo(saloph)CH_2CN$ complexes, the reactivity of the latter being estimated 10 times as large, when L = 3,5 lutidine. Correspondingly, the Co–N axial bond in saloph complexes are found to be 0.1 Å longer than those reported for cobaloximes having comparable axial ligand sets [1].

As already observed [6, 7] for cobaloximes the bonding to cobalt of the Et and Pr groups significantly affects their geometry, because of the steric interaction with the equatorial $(GH)_2$ ligand. For compound (**2**) the $\mathrm{Co{-}\widehat{C}H_2{-}Me}$ angle is opened to 119.9(7) and the C–Me bond length is shortened to 1.43(1) Å. For compound (**3**) the $\mathrm{Co{-}\widehat{C}H{-}Me}$ angles and the C–Me distances have mean values of 116.2(8) and 1.48(16) Å respectively, whereas the $\mathrm{Me\widehat{C}HMe}$ angle is 112(1) with a flattening of the tetrahedron around C(10). Although thermal motion may partially influence the above values, they are consistent with a significant change of hybridization at the carbon bonded to cobalt with respect, *e.g.*, to n-propane and isobutane. The relative orientation of the alkyl group with respect to the equatorial ligands is shown in Fig. 2 for compounds (**2**) and (**3**).

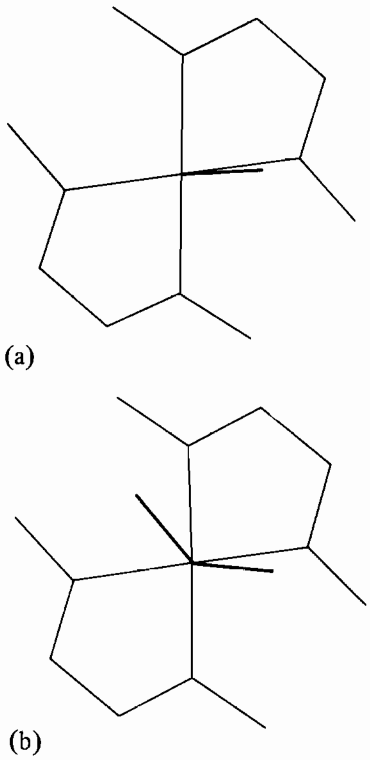

Fig. 2. Relative orientation of (a) the ethyl group in (**2**) and (b) of the i-propyl group in (**3**) with respect to the GH ligands.

Acknowledgements

This work was partly supported by a grant (to L.R.) from C.N.R. (Rome) and partly from a grant of Ministero Pubblica Istruzione, Rome, Italy. Work at Emory was supported by N.I.H. grant GM29225, U.S.A.

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