Journal of Organometallic Chemistry, 425 (1992) 131–139
Elsevier Sequoia S.A., Lausanne
JOM 22301

Evidence of steric influences on the Co–C bond lengths in vitamin B_{12} model compounds

II *. Crystal structures of two adamantylcobaloximes with the neutral ligands H_2O and PPh_2Et

Silvano Geremia [a], Lucio Randaccio [a,*], Ennio Zangrando [a]
and Luciano Antolini [b]

[a] *Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste (Italy)*
[b] *Dipartimento di Chimica, Università di Modena, 41100 Modena (Italy)*

(Received July 18, 1991)

Abstract

The structures of *trans*-Co(DH)$_2$adam(H$_2$O) (**1**) and *trans*-Co(D)(DH$_2$)adam(PPh$_2$Et) (**2**), where D = dianion of dimethylglyoxime, and adam = adamantyl group, are determined by X-ray crystal structure analysis. The Co–C bond lengths are 2.129(3) Å (**1**) and 2.217(7) Å (**2**). The α and d (measures of the geometrical deformation of the equatorial moiety) are −15.8° and −0.093 Å in **1** and −3.2° and −0.011 Å in **2**, respectively. These differences are ascribed to steric influences of the neutral ligand. Linear regression analyses of Co–C bond lengths with α and d in adamantylcobaloximes have confirmed that the axial-equatorial interactions are of considerable importance in these systems. The comparison between adamantyl- and methyl-cobaloximes suggests a higher elasticity of the Co–C(adam) bond compared to Co–C(Me).

Introduction

Alkylcobaloximes, Co(DH)$_2$RL, are octahedral complexes of cobalt(III), where DH's (monoanions of dimethylglyoxime) occupy all the equatorial positions, L is a neutral Lewis base, and R is an alkyl group. They have been widely investigated, both as simple models of vitamin B_{12} [1–4] and as a flexible organometallic system, because variation of L and R endows the complexes with different electronic and steric properties [2–4].

More than 100 of these complexes have been studied in solution and in solid state [3,4], providing not only some basic understanding of the nature of the Co–C bond [3], but also demonstrating some interesting relationships among solution and solid state properties [4,5]. The variations in the structures mainly concerned with the axial moiety R–Co–L, which are consistent with kinetic and spectroscopic

---

* For Part I see ref. 8.

features, have been interpreted in terms of electronic and steric influences of one axial ligand on the other, and on the equatorial moiety [4,5]. In particular, the Co–C bond length was related mainly to the bulk of R and, to a lesser extent, to the bulk of L. On the other hand, the Co–L distance increases with the σ-donor power of R and with the bulk of L. Further, the bending angle, α, between the planes passing through the two DH units and the displacement, d, of the Co atom from the plane of the four equatorial N donors, which vary by about 25° and 0.2 Å, respectively, have been attributed mainly to the relative bulks of the axial ligands [3,4]. However, it is not clear to what extent the Co coordination sphere in stable alkylcobaloximes may be strained. Some years ago [6], we reported a very long Co–C bond (2.154(5) Å) in $Co(DH)_2$adam 1-MeIm (1-MeIm = 1-methylimidazole, adam = adamantyl), the first determination of the length of Co to tertiary carbon atom bond. Later, longer values up to 2.214(3) Å were found in other $Co(DH)_2$adamL [7], with L = 4CN–py, Me_3Bzm (1,5,6-trimethylbenzimidazole), $P(OMe)_3$ or $P(O^iPr)_3$. The increases in the Co-adam bond lengths appeared to depend principally on the bulk of L.

Furthermore, in part I of this series [8] we observed that in complexes $Co(DH)_2$MeL there is an approximately linear relationship between the Co–C distances and the α or d parameters, supporting the idea that steric effects, influencing the Co coordination sphere, play a basic role in Co–C bond stability [1–4]. In Me derivatives the variation of Co–C distances, and α and d parameters with the bulk of L are small, and so it was of interest to confirm the above relationship in adamantyl series, where larger variations are found. In order to expand both the lower and upper limit of the adamantyl series, we have determined the structures of the derivatives with L = H_2O (**1**) and PPh_2Et (**2**).

Experimental

Prismatic crystals of **1** and **2** were selected for X-ray analysis. All intensity data were collected on a CAD4 Enraf–Nonius single crystal diffractometer at room temperature by the ω–2θ scan technique by using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). The intensities were corrected for Lorentz and polarization factors. An empirical absorption correction, based on the ψ scan, was applied to the data of **2**, but neglected for **1**, because of the almost isotropic crystal dimensions.

The two structures were solved by conventional Patterson and Fourier methods, and refined through full-matrix least-squares methods. The hydrogen atoms, located on F Fourier maps, were added as fixed contributions at their observed positions. The adamantyl group in **1** was found to be disordered in two different orientations, related approximately by a rotation of about 60° around the Co–C bond, with occupancy factors of 0.7 (C(10a)–C(18a)) and 0.3 (C(10b)–C(18b)). In **1** carbon atoms with lower occupancy and in **2** all carbons except methyl carbon atoms were refined isotropically. Least-squares refinement with unitary weight led to the final R and R_w values reported in Table 1. The final ΔF Fourier maps were featureless, with no peak higher than ± 0.2 and ± 0.3 e $Å^{-3}$, in **1** or **2**, respectively.

Complex neutral-atom scattering factors, including anomalous dispersion terms for all non-H atoms, were taken from *International Tables for X-Ray Crystallogra-*

Table 1

Crystallographic data and details of refinement for compounds **1** and **2**

	1	**2**
L	H_2O	PPh_2Et
Formula	$CoO_5N_4C_{18}H_{31}$	$CoPO_4N_4C_{32}H_{44}$
F.W.	442.4	638.7
a (Å)	29.221(3)	9.747(1)
b (Å)	13.264(1)	19.260(2)
c (Å)	10.678(1)	33.040(3)
β (deg)	98.28(1)	
V (Å^3)	4095.5	6202.5
Z	8	8
Space group	$C2/c$ (no. 15)	$Pbca$ (no. 61)
D(calc.) (g cm^{-3})	1.44	1.37
D(measured) (g cm^{-3})	1.50	1.38
μ(Mo-K_α) (cm^{-1})	8.7	5.9
No. measured reflections	6500	6473
No. independent reflections	3474 ($I \geq 3\sigma I$)	2511 ($I \geq 2\sigma I$)
R (F_o)	0.038	0.049
R_w (F_o)	0.041	0.050

phy [9]. The calculations were carried out on a VAX 2000 using the SDP package [10] for **1** and on a CRAY X-Mp/48 computer, using the SHELX76 system of programs [11] for **2**. Final non-H positional parameters and B_{eq} (Å^2) are given in Tables 2 and 3. Hydrogen atom coordinates, anisotropic thermal parameters, and a list of final calculated and observed structure factors, as well as a complete list of bond lengths and angles are available from the authors.

Results and discussion

ORTEP drawings [12] of molecules **1** and **2** with the non-H atom numbering scheme are depicted in Figs. 1 and 2, respectively. In both complexes, the dimethylglyoximate ligands occupy the four equatorial positions of a distorted octahedron around Co. The Co atom is displaced towards the adamantyl ligand out of the plane of the four N equatorial donors by −0.093 Å in **1** and −0.011 Å in **2**. The two chemically equivalent halves of the equatorial moiety are bent towards the H_2O ($\alpha = -15.8°$) in **1** and essentially coplanar in **2** ($\alpha = -3.2°$). The dihedral angle, α, was calculated by omitting oxygen and methyl carbon atoms that, being in terminal positions, may be influenced by packing forces [8]. A negative sign for α and d indicates bending towards the neutral ligand and displacement towards the adamantyl group, respectively. In **1** the hydrogen atoms of the oxime bridge involved in the hydrogen bond belong to different chelating groups, while in **2** they belong to the same unit of the equatorial moieties (Figs. 1 and 2). Molecule **1** with the usual H-bonding scheme [3] can be formulated as $Co(DH)_2adam(H_2O)$, whereas molecule **2** with a rare H-bonding scheme [13] can be described as $Co(D)(DH_2)adam(PPh_2Et)$. Nevertheless, in both compounds the geometry of the equatorial ligands is very close to that found in other cobaloximes [3,4]. The O–Co–C axial fragment is characterized by Co–O and Co–C distances

Table 2

Atomic coordinates for non-hydrogen atoms for compound **1** with esds in parentheses

Atom	x	y	z	B (Å^2) [a]
Co	0.33851(1)	0.31585(3)	0.18453(4)	1.881(5)
O(1)	0.28143(8)	0.1498(2)	0.0945(2)	2.84(4)
N(1)	0.28717(8)	0.2290(2)	0.1744(2)	2.17(4)
C(1)	0.2146(1)	0.1881(3)	0.2539(3)	3.49(7)
C(2)	0.2566(1)	0.2505(2)	0.2467(3)	2.38(5)
C(3)	0.2686(1)	0.3412(2)	0.3233(3)	2.40(5)
C(4)	0.2362(1)	0.3907(3)	0.3999(4)	4.00(8)
N(2)	0.30923(8)	0.3759(2)	0.3122(2)	2.18(4)
O(2)	0.32537(8)	0.4605(2)	0.3732(2)	2.87(4)
O(3)	0.39336(8)	0.4896(2)	0.2629(2)	3.21(5)
N(3)	0.38632(9)	0.4109(2)	0.1822(2)	2.39(5)
C(5)	0.4501(1)	0.4722(3)	0.0743(4)	4.06(8)
C(6)	0.4117(1)	0.4022(3)	0.0925(3)	2.56(6)
C(7)	0.3983(1)	0.3153(3)	0.0099(3)	2.61(5)
C(8)	0.4208(1)	0.2881(3)	−0.1033(3)	3.63(7)
N(4)	0.36463(9)	0.2646(2)	0.0456(2)	2.40(5)
O(4)	0.34799(8)	0.1827(2)	−0.0225(2)	3.09(4)
C(9)	0.3801(1)	0.2213(2)	0.3162(3)	2.25(5)
C(10a)	0.3491(2)	0.1461(4)	0.3775(5)	3.23(9)
C(11a)	0.4139(2)	0.1578(4)	0.2515(5)	3.5(1)
C(12a)	0.4071(2)	0.2850(4)	0.4187(5)	3.7(1)
C(13a)	0.4373(2)	0.2172(5)	0.5207(6)	4.7(1)
C(14a)	0.4061(2)	0.1463(5)	0.5758(5)	5.0(1)
C(15a)	0.3788(2)	0.0792(4)	0.4784(5)	4.0(1)
C(16a)	0.4130(2)	0.0199(4)	0.4099(6)	4.4(1)
C(17a)	0.4447(2)	0.0886(5)	0.3539(5)	4.4(1)
C(18a)	0.4700(2)	0.1570(5)	0.4497(6)	5.1(1)
C(10b)	0.4318(4)	0.2491(9)	0.319(1)	3.4(2) [b]
C(11b)	0.3671(4)	0.2391(8)	0.449(1)	2.8(2) [b]
C(12b)	0.3717(4)	0.1147(9)	0.278(1)	3.0(2) [b]
C(13b)	0.4013(5)	0.043(1)	0.371(1)	4.3(3) [b]
C(14b)	0.4502(6)	0.072(1)	0.358(2)	6.2(4) [b]
C(15b)	0.4631(5)	0.175(1)	0.409(1)	4.3(3) [b]
C(16b)	0.4500(5)	0.195(1)	0.536(1)	5.2(3) [b]
C(17b)	0.3982(4)	0.168(1)	0.546(1)	3.8(2) [b]
C(18b)	0.3911(5)	0.060(1)	0.499(1)	4.2(3) [b]
O(5)	0.29591(7)	0.4132(2)	0.0588(2)	2.69(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3\Sigma_i\Sigma_j a_i a_j \beta(i, j)$. [b] Atom refined isotropically.

of 2.130(2) and 2.129(3) Å, respectively, and by an O–Co–C angle of 177.8(1)°. In **2**, the Co–P and Co–C distances are 2.390(2) and 2.217(7) Å, respectively, and the P–Co–C angle is 176.9(2)°.

The geometry of the axial fragment O–Co–X in some aquacobaloximes is reported in Table 4. The H_2O ligand is very small and is a very poor electron-donor. In fact, the Co–C bond length, scarcely affected by steric and electronic influences of the *trans*-aqua ligand [3,14], is the shortest found in adamantyl derivatives (see below). Thus, the changes in geometry in aquacobaloximes, should reflect mainly the electronic and steric abilities of X. As expected the increase of the Co–O

Table 3

Atomic coordinates for non-hydrogen atoms for compound **2** with esds in parentheses

Atom	x	y	z	B (Å^2) [a]
Co	0.05066(7)	0.24970(7)	0.12807(2)	2.13(3)
O(1)	−0.1514(5)	0.3559(2)	0.1300(2)	3.9(2)
N(1)	−0.0668(6)	0.3181(3)	0.1067(2)	3.1(2)
C(1)	−0.152(1)	0.3783(4)	0.0460(3)	6.6(5)
C(2)	−0.0651(8)	0.3266(4)	0.0675(2)	3.5(1) [b]
C(3)	0.0290(7)	0.2800(4)	0.0479(2)	3.4(1) [b]
C(4)	0.056(1)	0.2774(4)	0.0030(2)	6.3(5)
N(2)	0.0957(6)	0.2390(3)	0.0732(1)	2.9(2)
O(2)	0.1942(5)	0.1952(2)	0.0601(1)	4.2(2)
O(3)	0.2523(6)	0.1430(2)	0.1268(2)	3.9(2)
N(3)	0.1693(6)	0.1833(3)	0.1494(2)	2.8(2)
C(5)	0.256(1)	0.1229(4)	0.2095(3)	5.4(4)
C(6)	0.1707(7)	0.1766(3)	0.1885(2)	3.3(1) [b]
C(7)	0.0772(7)	0.2241(3)	0.2088(2)	3.1(1) [b]
C(8)	0.0609(8)	0.2294(4)	0.2532(2)	5.0(4)
N(4)	0.0069(5)	0.2605(3)	0.1827(1)	2.7(2)
O(4)	−0.0893(5)	0.3050(2)	0.1964(1)	3.7(2)
C(9)	−0.1108(7)	0.1691(3)	0.1231(2)	2.5(1) [b]
C(10)	−0.1504(8)	0.1429(3)	0.1652(2)	3.5(1) [b]
C(11)	−0.2393(8)	0.1992(3)	0.1032(2)	3.5(1) [b]
C(12)	−0.0589(8)	0.1086(3)	0.0980(2)	3.6(1) [b]
C(13)	−0.2617(8)	0.0861(4)	0.1622(2)	3.8(1) [b]
C(14)	−0.2053(8)	0.0265(4)	0.1372(2)	4.3(2) [b]
C(15)	−0.1728(7)	0.0511(4)	0.0948(2)	3.8(1) [b]
C(16)	−0.2986(8)	0.0827(4)	0.0755(2)	4.1(1) [b]
C(17)	−0.3539(8)	0.1427(4)	0.1005(2)	3.7(1) [b]
C(18)	−0.3879(8)	0.1179(4)	0.1426(2)	3.8(1) [b]
P	0.2236(2)	0.33622(9)	0.13736(6)	2.44(7)
C(19)	0.1882(6)	0.3916(3)	0.1806(2)	2.5(1) [b]
C(20)	0.2527(9)	0.3818(4)	0.2179(2)	3.2(1) [b]
C(21)	0.2121(7)	0.4182(3)	0.2522(2)	3.6(1) [b]
C(22)	0.1048(7)	0.4650(3)	0.2497(2)	3.6(1) [b]
C(23)	0.0385(7)	0.4747(3)	0.2138(2)	3.2(1) [b]
C(24)	0.0774(7)	0.4380(3)	0.1795(2)	2.9(1) [b]
C(25)	0.2622(7)	0.3936(3)	0.0944(2)	2.9(1) [b]
C(26)	0.2354(8)	0.4649(4)	0.0942(2)	4.1(1) [b]
C(27)	0.2777(8)	0.5023(5)	0.0599(2)	4.3(2) [b]
C(28)	0.3347(9)	0.4726(4)	0.0272(2)	5.0(2) [b]
C(29)	0.3595(9)	0.4020(4)	0.0276(2)	4.6(2) [b]
C(30)	0.3220(7)	0.3628(4)	0.0611(2)	3.7(1) [b]
C(31)	0.3932(7)	0.2992(3)	0.1478(2)	3.3(1) [b]
C(32)	0.5121(7)	0.3507(4)	0.1510(3)	4.5(4)

[a] See Table 2. [b] Atom refined isotropically.

distance (about 0.2 Å) changing from py to adam parallels the increase of the σ-donating ability of X. On the other hand, the d and α values become more negative with increasing bulk of X.

The Co–C distance, and α and d values for several adamantylcobaloximes with different L ligands are given in Table 5, together with the corresponding values for the methyl analogues. The Co–C bond lengths vary by about 0.1 Å going from

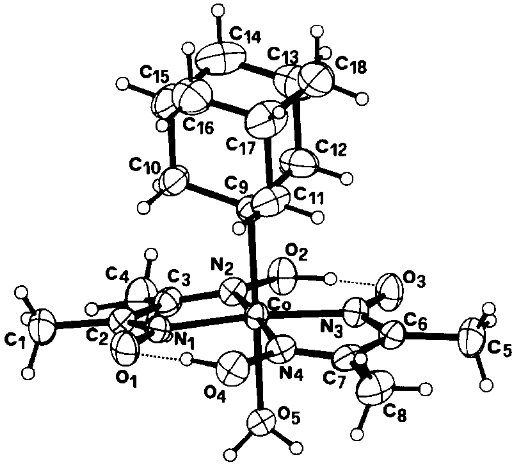

Fig. 1. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for non-hydrogen atoms of **1**. Only the orientation of the adamantyl group of higher occupancy is shown.

L = H_2O (2.129(3) Å) to L = PPh_2Et (2.217(7) Å). Such a difference is probably the maximum for this bond as a function of the bulk of L, for adamantylcobaloximes stable enough to be structurally characterized. The α and d values, both in the adamantyl and the methyl series, indicate that aqua is the smallest and phosphine is the biggest ligand among those of Table 5. The values become less negative in the adamantyl series and more positive in the Me series as L changes from H_2O to phosphine, with values close to zero when L is large (adamantyl) or

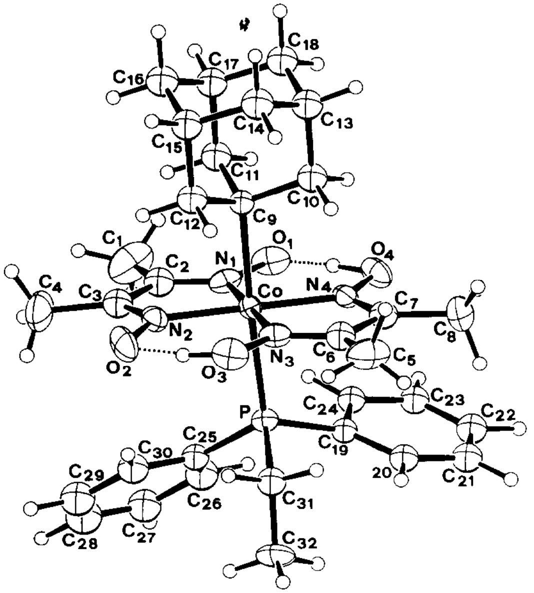

Fig. 2. ORTEP drawing (50% probability thermal ellipsoids) and labeling scheme for non-hydrogen atoms of **2**.

Table 4

Geometry of the axial fragment O–Co–X in some complexes $Co(DH)_2X(H_2O)$ [a] (data from refs. 3 and 4 unless otherwise stated)

X	Co–O (Å)	Co–X (Å)	O–C–X (°)	α (°)	d (Å)	Refcode [b]
H_2O	1.900(4)	1.900(4)	180.0(2)	0	0.000	SANMEZ
py [c]	1.916(3)	1.926(3)	178.8(1)	−5.7	−0.040	FORLED
NO_2	1.980(5)	1.881(2)	179.0(2)	−7.0	−0.048	NMGCOB10
CN	1.992(4)	1.906(5)	179.9(2)	−2.9	−0.017	BUPHID
CH_2CMe_3	2.056(5)	2.044(7)	172.4(3)	−6.9	−0.043	BEDPOP
Me	2.055(8)	1.978(11)	178.0(3)	−4.4	+0.001	AMGXCO01
	2.058(3)	1.990(5)	178.0(2)	−4.6	−0.002	AMGXCO
adam [d]	2.130(2)	2.129(3)	177.8(1)	−15.8	−0.093	

[a] For the sign of α and d, see text. [b] Refcodes [15] from Cambridge Structural Database. [c] Ref. 14. [d] Present work.

small (methyl). Linear regression analysis of the Co–C(adam) bond distances against α and d of Table 5 (Fig. 3) give the eqs. 1 and 2, respectively (r is the corresponding correlation coefficient)

$$\text{Co–C} = 2.246(13) + 0.0080(14)\alpha \quad r = 0.908 \tag{1}$$

$$\text{Co–C} = 2.215(10) + 0.95(12)d \quad r = 0.946 \tag{2}$$

The linear regressions for the adamantyl series give correlation factors higher than those found for the methyl derivatives (0.839 and 0.742 for α and d, respectively) [8]. Moreover, the slope coefficients are about 2.6 times greater than those derived in methyl series [8]. This shows a higher flexibility of the Co–C bond in adamantyl derivatives, consistent with a weaker bond.

Table 5

Co–C (Å) bond lengths, α (°) [a] and d (Å) [a] values for adamantylcobaloximes. The values for methyl analogues are reported for comparison (data from refs. 3 and 4, unless otherwise stated)

L	R = adam				R = Me			
	Co–C (Å)	α (°)	d (Å)	Refcode	Co–C (Å)	α (°)	d (Å)	Refcode [b]
H_2O [c]	2.129(3)	−15.8	−0.093		1.978(11)	−4.4	+0.001	AMGXCO01
					1.990(5)	−4.6	−0.002	AMGXCO
1-MeIm	2.154(5)	−9.7	−0.057	COJBOS	2.009(7)	+4.1	+0.061	MGXIMC
NH_2Ph [d]	2.155(4)	−10.2	−0.069	KAWRIJ	1.992(2)	+3.8	+0.035	
	2.162(4)	−9.7	−0.061					
py [e]	2.160(4)	−10.6	−0.047	DIDJEF	1.998(5)	+1.6	+0.054	GXMPYC10
Me_3Bzm	2.179(5)	−7.5	−0.027	FOWCID	1.989(2)	+3.0	+0.056	
$P(O^iPr)_3$	2.199(6)	−7.3	−0.006	DIDHUT				
$P(OMe)_3$	2.214(3)	−7.2	−0.015	DIDHON	2.014(14)	+10.2	+0.093	
PPh_2Et [c,f]	2.217(7)	−3.2	−0.011		2.026(6)	+11.2	+0.111	MGLPCO

[a] For the sign of α and d, see text. [b] Refcodes [15] from Cambridge Structural Database. [c] Present work. [d] The values refer to two crystallographically independent molecules. [e] For the adamantyl derivative L = $4\text{-}Me_2N\text{-}py$. [f] For the methyl derivative, L = PPh_3.

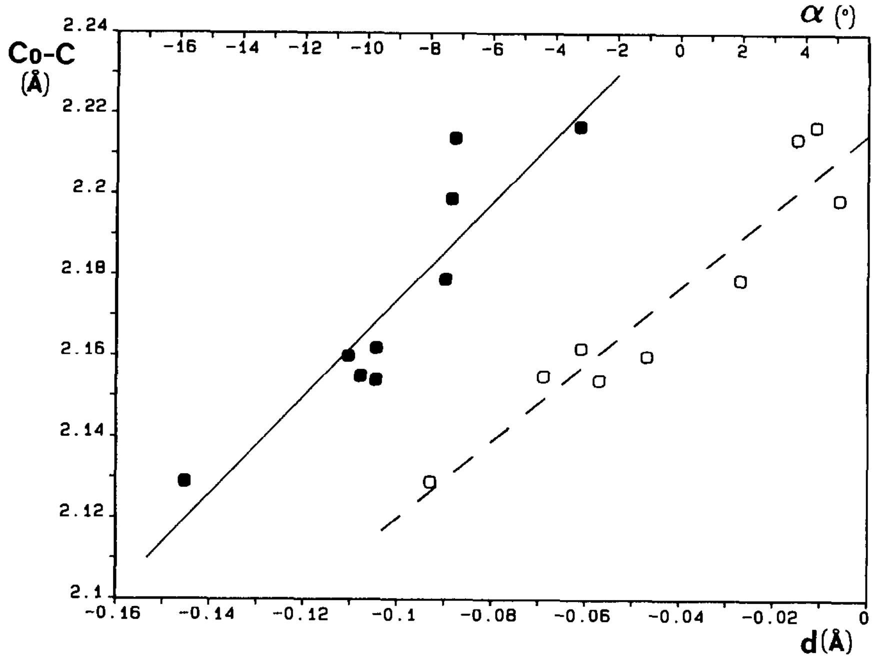

Fig. 3. Plots of Co–C(adam) distances against *α* and *d* for cobaloximes of Table 5. Full points refer to *α* (upper scale) and open points to *d* (lower scale).

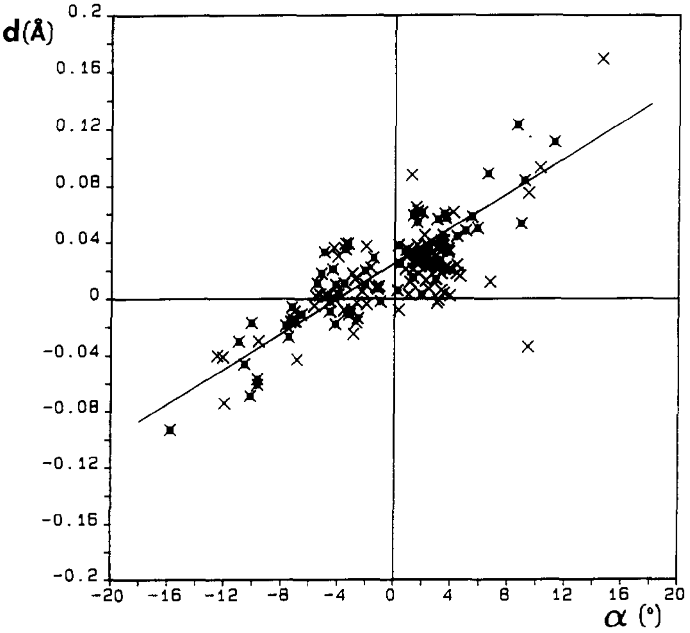

Fig. 4. Plot of *α* against *d* for alkylcobaloximes. The linear regression includes only data relative to structures with average esd of C–C bonds below 0.010 Å, marked with solid circles.

Since eqs. 1 and 2 have different intercepts, it seemed worthwhile to investigate this discrepancy by a correlation analysis of the α and d values of 140 alkylcobaloximes retrieved from the Cambridge Structural Database (CSD) [15]. The linear regression, limited to 70 points *, has the following equation:

$$d = 0.025(18) + 0.0062(4)\alpha, \quad r = 0.785 \tag{3}$$

The corresponding diagram is given in Fig. 4, where d values are plotted against α values. Equation 3 confirms a small but positive value for d (0.025(18) Å) when $\alpha = 0$, i.e. when the equatorial ligand is planar. Since α is expected to be zero for axial ligands with comparable bulk, the slight displacement of Co towards L may be interpreted as showing that Co is more tightly bound to L than to the alkyl group.

Acknowledgements

We thank Professor L.G. Marzilli (Atlanta, GA) for kindly supplying the crystals, and CNR (Rome) and MURST (Rome) for financial support.

References

1 J. Halpern, Science, 227 (1985) 869 and refs. therein; J.H. Pratt, Chem. Soc. Rev., 14 (1985) 161; B.P. Hey and R.G. Finke, J. Am. Chem. Soc. 109 (1987) 8012 and refs. therein.

2 F.T.T. Ng, G.L. Rempel, C. Mancuso and J. Halpern, Organometallics, 9 (1988) 2762 and refs. therein.

3 N. Bresciani Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers and P.J. Toscano, Coord. Chem. Rev., 63 (1985) 1.

4 L. Randaccio, N. Bresciani Pahor, E. Zangrando and L.G. Marzilli, Chem. Soc. Rev., 18 (1989) 225.

5 N. Bresciani Pahor, S. Geremia, C. Lopez, L. Randaccio and E. Zangrando, Inorg. Chem., 29 (1990) 1043.

6 N. Bresciani Pahor, L.G. Marzilli, L. Randaccio, P.J. Toscano and E. Zangrando, J. Chem. Soc., Chem. Commun. (1984) 1508.

7 N. Bresciani Pahor, L. Randaccio, E. Zangrando and P.A. Marzilli, J. Chem. Soc., Dalton Trans., (1989) 1941 and refs. therein.

8 S. Geremia, M. Mari, L. Randaccio and E. Zangrando, J. Organomet. Chem., 408 (1991) 95.

9 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, U.K., 1979.

10 B.A. Frenz, Enraf–Nonius Structure Determination Package, 4th ed., Delft, Netherlands, 1980.

11 G.M. Sheldrick, SHELX76, Program for Crystal Structure Determination, University of Cambridge, Cambridge, UK, 1976.

12 C.K. Johnson, ORTEP, Report ORNL 3794, National Laboratory, Oak Ridge, TN, 1965.

13 L.G. Marzilli, F. Bayo, M.F. Summers, L. Brannon Thomas, E. Zangrando, N. Bresciani Pahor, M. Mari and L. Randaccio, J. Am. Chem. Soc., 109 (1987) 6045.

14 M.W. Attia, E. Zangrando, L. Randaccio and C. Lopez, Acta Crystallogr., C43 (1987) 1521.

15 F.H. Allen, S.A. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Roger and D.G. Watson, Acta Crystallogr., Sect. B, 35 (1979) 2331; CSD 4.4 version of January 1991 with 86026 entries.

---

* The linear regression includes only structures with average esd of C–C bonds below 0.010 Å. Data utilized in the correlation analysis are available from the authors.