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Note

On an unusual shortening of the $C(sp^3)-C(sp^3)$ bonds in n-propylcobaloximes

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Abstract

The structures of two n-propyl cobaloximes, $[(n-Pr)Co(Hdmg)_2(L)]$ ·H₂O where $L = H_2O$ (6) and NH₂Ph (7), and Hdmg = monoanion of dimethylglyoxime, are described. The large static disorder undergone by the n-propyl group is attributed to different conformations of n-Pr, differing in the torsional angle around the axial Co-L bond. This result contrasts with those reported for the anhydrous $[(n-Pr)Co(Hdmg)_2(H_2O)]$ (1) derivative and its inclusion compound with α -cyclodextrin (2), where a significant lengthening of 0.16 Å in the C α -C β bond of n-Pr in 2, with respect to an incredibly short bond in 1, was attributed to the interaction of the cobaloxime with α -cyclodextrin. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently, a paper describing the preparation and structure of the cobaloxime (n-Pr)Co(Hdmg)₂(H₂O) (1), where Hdmg = monoanion of dimethylglyoxime, and of its inclusion compound with α -cyclodextrin (α -cd) (2) has been reported [1]. Interestingly, the structural analysis showed that the compound 2 is formed by the inclusion of the cobaloxime n-Pr group into the hydrophobic cavity of α -cd. The authors have found by comparison with the geometry of 1 with that of the cobaloxime moiety in 2, some obvious conformational changes: (a) the displacement of Co out of the four N donor plane towards the alkyl group is 0.008 Å in 1 and 0.038 Å in 2; (b) the two equatorial Hdmg units make an interplanar angle of 1° in 1 and of 10° in 2; (c) in 2 the axial Co-OH₂ bond is lengthened by 0.02 Å, whereas the C–Co–O angle is narrowed by 3.5° ; (d) the n-Pr C α -C β distance, which is unexpectedly short for a $C(sp^3)-C(sp^3)$ single bond (1.237(13) Å) in 1, is found

to be lengthened by 0.16 Å in 2, while the Co-C-C angle is widened by 5° in 2. However, no significant change was observed in the Co-C distances. More recently, Luo et al. [2] have reported also the structure of (i-But)Co(Hdmg)₂(H₂O) (3) and of its inclusion compounds with $(\alpha$ -cd) (4) and $(\beta$ -cd) (5). Distortions similar to (a)–(c) were observed, but the i-Bu $C\alpha$ –C β distances in 3-5 are quite normal, whereas the C β -Me distances in 5 were found to be 1.34(1) and 1.24(1) Å, respectively. The authors ascribed [1] the observed differences (a)-(d) in 2, to the hydrophobic interaction between the n-Pr group and the α -cd cavity and to the steric interaction between the α -cd rim and the cobaloxime equatorial moiety. That such interactions are responsible for the geometrical changes (a)-(c) is convincing, but that they can provoke the dramatic change of the C α -C β distance from 1.237(13) Å in 1 to 1.394(7) Å in **2** is highly questionable. In fact, recent molecular mechanics calculations [3] reproduced satisfactorily bond lengths and angles in 1 and 2, except for the C α -C β distance calculated to be 1.536 Å. The analysis of the anisotropic thermal factors of the atoms in the two structures shows high values (about four times those of the other atoms) of U_{22} in 1 and of U_{11}

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in 2 for the β -carbon atom, and an orientation of the corresponding axis of the thermal ellipsoids nearly parallel to the coordination plane. This observation suggests that the unusual geometry of n-Pr in 1 and 2 might be the result of a mathematical artefact, due to the refinement, carried out without taking into account a possible static disorder of the alkyl moiety. In spite of the large number of structurally characterized alkylcobaloximes [4], to our knowledge no structural data for an n-propylcobaloxime are available for comparison. Therefore, we tried to check the static disorder hypothesis, redoing the structural analysis of 1. Unfortunately, we were not able to obtain any single crystal following the method described in Ref. [1]. However, good quality single crystals of the mono-hydrated form of 1, $[(n-Pr)Co(Hdmg)_2(H_2O)] \cdot H_2O$ (6), were obtained. The structures of **6** and that of the $[(n-Pr)Co(Hdmg)_2-$ (PhNH₂)]·H₂O analogue (7), were determined.

2. Experimental

2.1. Synthesis

2.1.1. $[(n-Pr)Co(Hdmg)_2(H_2O)] \cdot H_2O$ (6)

The complex $(n-Pr)Co(Hdmg)_2(Py)$, prepared as previously reported [5], was eluted through a column of acidic resin to obtain the corresponding aquo complex **6**. Red-brown crystals, suitable for structure determination were obtained by evaporation of a watermethanol solution in the dark. (Found: C, 35.4; H,

Table 1

Crystal data and structure refinement for 6 and 7

6.90; N, 15.1. Calc. for $C_{11}H_{25}N_4O_6Co$: C, 35.8; H, 6.84; N, 15.2%.)

2.1.2. $[(n-Pr)Co(Hdmg)_2(PhNH_2)] \cdot H_2O$ (7)

A water-methanol solution of **6**, obtained as above, was treated with an excess of aniline under stirring at room temperature (r.t.). Crystals of the complex were obtained by partial evaporation of the solvent and collected by filtration. (Found: C, 45.8; H, 6.95; N, 15.5. Calc. for $C_{17}H_{30}N_5O_5Co$: C, 46.0; H, 6.82; N, 15.8%.)

2.2. Crystal structure analyses

Intensity data for 6 and 7 were collected on an Enraf-Nonius CAD4 four-circle automated diffractometer with graphite-monochromated Mo Ka radiation. Accurate unit cell parameters and orientation matrix were determined by least-squares refinement of the setting angles of 25 well-centered reflections in the range $22 < 2\theta < 28^\circ$. Reflections were collected at r.t. in $\omega/2\theta$ scan mode. No decay throughout the data collection was observed. Correction for Lorentz-polarization and φ -scan absorption was applied. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares method (on F^2). The H atoms were not refined, but included at calculated positions in the final refinement for all the atomic species with full occupancy. Crystal, collection and refinement data are given in Table 1. The programs used are given in Refs. [6,7].

Compound	6	7
Empirical formula	C ₁₁ H ₂₅ CoN ₄ O ₆	C ₁₈ H ₃₂ CoN ₅ O ₆
Formula weight	368.28	473.42
<i>T</i> (K)	293(2)	293(2)
λ (Å)	0.7107	0.7107
Crystal system, space group	monoclinic, $C2/c$	triclinic, $P\overline{1}$
a (Å)	12.922(3)	8.465(1)
b (Å)	12.762(1)	11.383(1)
<i>c</i> (Å)	20.982(8)	12.869(2)
α (°)	90	77.08(1)
β (°)	99.83(3)	84.79(1)
γ (°)	90	70.75(1)
V (Å ³)	3409(2)	1140.9(2)
$Z, \rho_{\text{calc}} (\text{Mg m}^{-3})$	8, 1.435	2, 1.378
μ (Mo K α) (mm ⁻¹)	1.038	0.794
F(000)	1552	500
Crystal size (mm)	$0.5 \times 0.4 \times 0.2$	0.7 imes 0.7 imes 0.5
θ range (°)	2.26–29.96	2.26–29.98
Reflections collected/unique	$5095/4969 \ [R_{\rm int} = 0.040]$	$6886/6613 \ [R_{\rm int} = 0.029]$
Refinement method	full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4969/10/201	6613/14/283
Goodness-of-fit on F^2	1.062	1.054
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.060, \ wR_2 = 0.169$	$R_1 = 0.052, \ wR_2 = 0.176$



Fig. 1. ORTEP drawing with numbering scheme for the non hydrogen atoms of (a) $[(n-Pr)Co(Hdmg)_2(H_2O)]\cdot H_2O$ (6), and (b) $[(n-Pr)Co(Hdmg)_2(PhNH_2)]\cdot H_2O$ (7).

3. Results and discussion

The ORTEP drawings, obtained by anisotropic refinement of all the non-H atomic species of 6 and 7, all with occupancy factor 1, are given in Fig. 1. The refined geometry of the Co–n-Pr moiety in 6 ($R_1 = 0.057$) and 7 ($R_1 = 0.052$) is very close to that of 1 and 2 (Table 2) as well as the trend of the thermal factors. The U_{22} value for C β in **6** and those of almost all the U_{ii} of C β and $C\gamma$ in 7 are dramatically larger than the others, as shown also by the C β thermal ellipsoids of Fig. 1, whose longer axis is nearly parallel to the Co coordination plane. Among several tentative models, the most suitable appeared to be that in which C β and C γ were split over two positions C101, C102 and C111, C112, respectively, with half occupancy factors, corresponding to two orientations of the n-Pr group with respect to the equatorial moiety (Fig. 2a). In 7, the disorder of n-Pr, which is more severe than that in 6, was interpreted by assuming three different conformations of occupancies 0.4, 0.3 and 0.3, respectively (Fig. 2b),

Comparison of the geometry of the n-Pr–Co–OH₂ fragment in 1, 2, 6 and 7 after the anisotropic refinement with all the non-hydrogen atoms with full occupancy

	1	2	6	7
Bond distances (Å))			
Co–OH ₂ (NH ₂ Ph)	2.063(4)	2.083(2)	2.069(3)	2.142(3)
Co–Ca	2.008(8)	2.013(4)	2.010(4)	2.017(4)
Cα–Cβ	1.237(12)	1.394(7)	1.335(8)	1.247(13)
Cβ–Cγ	1.509(13)	1.550(7)	1.526(8)	1.579(12)
Bond angles (°)				
Co–Cα–Cβ	129.3(7)	124.1(3)	125.5(5)	127.1(7)
Cα–Cβ–Cγ	126.0(9)	117.1(4)	117.9(6)	116.0(10)



(b)

Fig. 2. Sketches showing the static disorder of the n-Pr group in (a) $[(n-Pr)Co(Hdmg)_2(H_2O)] \cdot H_2O$ (6), and (b) $[(n-Pr)Co(Hdmg)_2-(PhNH_2)] \cdot H_2O$ (7).

Table 3 Co–C and Co–L axial distances (Å) in aquo and aniline alkylcobaloximes $^{\rm a}$

R	$L = H_2O$		L = PhNH	[₂	
	Со–О	Co–R	Co–N	Co–R	
L	1.900(4)	1.900(4)	2.009(5)	2.007(5)	
Me	2.058(3)	1.990(5)	2.129(1)	1.992(2)	
Et			2.147(2)	2.030(3)	
n-Pr ^b	2.067(3)	1.998(4)	2.139(3)	1.986(3)	
n-Pr ^c	2.063(4)	2.008(8)			
i-Bu ^d	2.052(2)	2.011(3)			
i-Pr			2.177(2)	2.068(3)	
CH ₂ CMe ₃	2.056(5)	2.044(7)			
Adamantyl ^e	2.130(2)	2.129(3)	2.215(4)	2.159(4)	

^a Data are from Ref. [4] if not otherwise stated.

^b Present work.

° Ref. [1].

^d Ref. [2].

^e Ref. [8].

Table 4

Axial distances (Å) in [(R)Co(dmgH)_2(PX_3)], with R = Cl and Me and in compounds 1–6 $^{\rm a}$

	Co–Cl	Co–P	Co–Me	Со–Р
P(OMe) ₃	2.280(5)	2.188(4)	2.01(1)	2.256(4)
$P(Me)_3$			2.015(3)	2.293(1)
P(OMe) ₂ Ph	2.288(2)	2.213(2)	2.013(5)	2.287(1)
P(OMe)Ph ₂	2.290(1)	2.242(1)	2.019(6)	2.352(1)
P(n-But) ₃	2.294(2)	2.265(2)		
PPh ₃	2.287(2)	2.330(2)	2.026(6)	2.418(1)
PChx ₃	2.294(5)	2.369(5)	2.016(5)	2.463(1)
Compound	Со–О	Co–C		
1 ^b	2.063(4)	2.008(8)		
6 °	2.067(3)	1.998(4)		
2 ь	2.083(2)	2.011(3)		
3 ^d	2.052(2)	2.011(3)		
4 ^d	2 1 59(3)	2.016(4)		
	2.137(3)	_		

^a Data are from Ref. [4] if not otherwise stated.

^b Ref. [1].

^c Present work.

^d Ref. [2].

essentially differing by the torsion angle around Co– C9. The refinement was then performed with the Co– C α -C β and C α -C β -C γ angles fixed at about 118 and 110°, respectively, and the C–C distances about 1.54 Å. All the non-H atomic species were refined anisotropically, whereas the C β and C γ fractional species were treated isotropically. The final R_1 values were 0.060 for **6** and 0.052 for **7**. The refined conformations in **6** were characterized by N1–Co–C α -C β and Co–C α -C β -C γ torsion angles of 106.6(7) and –174.3(7)°, respectively, in one conformation and of 144(1) and –17.3(8)° in the other. The corresponding figures are 95.7(9), 174.4(6); -173.1(1.0), -176.7(8); 142.9(9), 179.8(1.1)° for the three conformations in the n-Pr group in 7. It is likely that similar results could be obtained by refining the structures of 1 and 2, using this procedure. On this basis, it appears clear that the observed abnormal C α -C β shortenings in 1 and 2 are due to a severe static disorder of the alkyl group and, hence, the observed change in the C-C distance in 1 and 2 reflects essentially the different degree of conformational disorder. Therefore, the observed lenghtening (*d*) should be essentially originated by a minor conformational freedom of n-Pr in 2, determined by the interaction with the cavity.

The disorder affects only the geometry of the alkyl group. In fact, the geometries of the $Co(Hdmg)_2(H_2O)$ moiety and of the H₂O-Co-C fragment in 1, 6 and 7 compare well. The butterfly α angle and the displacement d of Co out of four equatorial N-donors in **6** are $0.9(3)^{\circ}$ and -0.001(2) Å, and $4.2(3)^{\circ}$ and 0.034(1) Å in 7, and do not differ significantly from the values reported in 1. Analogously, the Co-C and Co-OH₂ (Co-N in 7) axial distances fit well the trends of the trans and cis influences in the series of aquo and aniline alkylcobaloximes (Table 3). In both crystals the water crystallization molecules are hydrogen-bonded to O3 and to an oxygen atom of another symmetry related water molecule (O2w-O3 = 2.830(5), O2w-O4' =2.866(5) Å in 6 and O1w-O3 = 2.823(5), O1w-O2' =2.869(5) Å in 7). The work presented in Ref. [1], in our opinion, gives a new and original contribution to cobaloxime chemistry. Our aim is only to stress that the crystallographic results, as obtained by the *automatic* refinement of the diffraction pattern, must be carefully evaluated and interpreted, especially when crystallographic results are used to formulate conclusions of chemical interest.

In order to interpret the lengthening of the $Co-OH_2$ bond and the constancy of the Co-C bond upon inclusion of the n-Pr cobaloxime, Luo et al. have suggested that the 'capped' a-cd behaves as a bulky R group above the Co(Hdmg)₂ moiety. In fact, the α -cd bends the equatorial moiety towards the trans ligand and provokes a lengthening of the Co-OH₂ distance (steric trans influence), according to the previous findings in cobaloximes [4]. However, the cd-cobaloxime interactions influence only the Co-OH₂ axial distances in the inclusion compounds, whereas the interactions between bulky R (or L) ligands and the equatorial moiety in cobaloximes, when the trans ligand has a small bulk, affect essentially the Co-R (or Co-L) bond (steric cis influence). This is shown in Table 4, where the axial distances in the two series RCo(dmgH)₂PX₃, with R = Cl and Me, are reported. In each series the Co-R distance does not vary appreciably, whereas the Co-P bond increases significantly with the increase in bulk of PX₃. In 2, the claimed increase in bulk of the alkyl group, due to the capped cd, does not determine

a detectable steric *cis* influence in the inclusion compounds (Table 3). Therefore, the apparently reasonable suggestion [1] that the observed strain of the Co–OH₂ bond upon inclusion, without lengthening of the Co–C bond, does not appear to be consistent with a merely factual enhancement of the alkyl group bulk induced by the cyclodextrin. More likely, it appears that the cobaloxime–cyclodextrin interactions provoke a 'soaking' of the alkyl group without perturbing the Co–C bond, probably because the Co–C strain requires energy higher than that necessary to bend the cobaloxime equatorial moiety and to lengthen the *trans* Co–OH₂ bond.

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