

Preliminary communication

STRUCTURAL FEATURES OF THE Co—C BOND IN ALKYLCOBALOXIMES. THE X-RAY STRUCTURE OF *trans*-BIS(DIMETHYLGLYOXIMATO) (VINYL)- (PYRIDINE) COBALT (III)

NEVENKA BRESCIANI-PAHOR, MARIO CALLIGARIS and LUCIO RANDACCIO*

Istituto di Chimica, Università di Trieste, 34127 Trieste (Italy)

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Summary

The X-ray crystal structural analysis of the title compound has shown that the vinyl group is σ -bonded to the cobalt atom. The Co—C distance of 1.966(6) Å is shorter than that in the analogous methyl derivative mainly because of the different carbon σ -covalent radii. The Co—N bond length of 2.073(3) Å is indicative of a strong *trans*-influence of the vinyl group, comparable with that of the methyl group. The Co atom lies 0.04 Å out of the plane of the four N-donors, being displaced towards the Py molecule. The two DH units are slightly bent (6.3°) away from the pyridine ligand.

The study of the Co—C bond in alkylcobaloximes is of interest for understanding the factors affecting its cleavage in such compounds, which are accepted as models of the vitamin B₁₂ coenzyme. Previous work has shown that the methyl group exerts a strong *trans* influence on the L axial ligand in systems such as MeCo(DH)₂L, where L = Py, *N*-methylimidazole, H₂O, PPh₃ [1, 2, 3]. In contrast, the Co—CH₃ bond length varies only from 1.990(5) [2] to 2.026(6) Å [3].

On the other hand it has been recently shown that the Co—C bond length increases with increasing bulkiness of the alkyl group bonded to the cobalt atom. In Me₂CHCo(DH)₂Py the Co—C distance is 2.085(3) Å [4]. These results indicate that the nature of the σ -bonded organic group may influence the Co—C bond to a significant extent. In order to establish whether structural changes may occur in potential π -acceptor ligands we determined the crystal structure of the vinyl derivative, CH₂=CHCo(DH)₂Py (I) (DH = dimethylglyoximato).

The crystals of I are orthorhombic, space group *P*2₁2₁2₁ with cell parameters, *a* 7.697(6), *b* 28.18(1), *c* 8.344(6) Å, *Z* = 4 and *D*_t 1.45 g/cm³. The structure was refined to *R* = 0.037 for 1559 independent reflexions ($\vartheta_{\max} \leq 26^\circ$) having intensities above 3 σ level and collected on a Siemens AED diffractometer, using

TABLE 1
BOND LENGTHS (Å) AND RELEVANT COORDINATION BOND ANGLES (°) AND ATOMIC COORDINATES

	X			Y			Z		
Co-N(1)	1.881(5)	C(5)-C(6)	1.487(8)	Co	318(1)	1397(0)	2427(1)		
Co-N(2)	1.872(5)	C(6)-C(7)	1.464(8)	O(1)	2876(6)	845(2)	869(6)		
Co-N(3)	1.895(4)	C(7)-C(8)	1.508(9)	O(2)	-3020(6)	1680(2)	1281(6)		
Co-N(4)	1.882(4)	N(5)-C(9)	1.398(7)	O(3)	-2211(5)	1969(1)	3969(6)		
Co-N(5)	2.073(3)	N(5)-C(13)	1.331(7)	O(4)	3716(5)	1164(2)	3548(6)		
Co-C(14)	1.966(6)	C(9)-C(10)	1.361(9)	N(1)	1279(7)	1025(2)	779(6)		
N(1)-O(1)	1.332(7)	C(10)-C(11)	1.415(12)	N(2)	-1332(6)	1430(2)	974(5)		
N(1)-C(2)	1.313(8)	C(11)-C(12)	1.356(11)	N(3)	-609(5)	1793(1)	4051(5)		
N(2)-C(3)	1.299(7)	C(12)-C(13)	1.353(8)	N(4)	2305(5)	1400(2)	3861(5)		
N(3)-O(3)	1.331(5)	C(14)-C(15)	1.176(15)	N(5)	-759(5)	802(1)	3498(5)		
N(3)-C(6)	1.298(7)	C(14)-C(152)	1.122(14)	C(1)	857(13)	889(3)	-1938(9)		
N(4)-O(4)	1.365(6)	N(1)-Co-N(2)	81.6(2)	C(2)	299(9)	972(2)	-497(6)		
N(4)-C(7)	1.284(7)	N(1)-Co-N(4)	99.4(2)	C(3)	-1365(9)	1206(2)	-378(7)		
C(1)-C(2)	1.505(10)	N(2)-Co-N(3)	98.5(2)	C(4)	-2723(11)	1201(3)	-1647(9)		
C(2)-C(3)	1.444(9)	N(3)-Co-N(4)	80.4(2)	C(5)	-115(9)	2198(2)	6632(8)		
C(3)-C(4)	1.488(10)	N(5)-Co-C(14)	178.1(2)	C(6)	366(8)	1888(2)	5266(6)		
				C(7)	2078(7)	1654(2)	5133(6)		
				C(8)	3519(9)	1722(3)	6838(8)		
				C(9)	195(8)	416(2)	3813(7)		
				C(10)	-434(11)	24(2)	4568(8)		
				C(11)	-2203(12)	26(3)	5029(8)		
				C(12)	-3176(9)	413(2)	4673(9)		
				C(13)	-2419(7)	788(2)	3941(7)		
				C(14)	1262(10)	1971(2)	1410(7)		
				C(15)	2583(16)	2078(5)	802(15)		
				C(152)	766(25)	2325(4)	998(18)		

Mo- K_{α} radiation. No absorption correction was applied (μ 10.2 cm $^{-1}$, 0.01 $< r_{\text{cryst.}} < 0.02$).

The molecular geometry of I is shown in Fig. 1, where the two orientations of the vinyl group with respect to the equatorial ligand are also shown. After refinement, populations of 0.6 and 0.4 were assigned to C(15₁) and C(15₂) atoms respectively. The four N donor atoms are coplanar within ± 0.007 Å with the cobalt atom displaced by 0.044 Å above their mean plane towards the pyridine molecule. The two DH moieties make an angle of 6.3°. Both pyridine and vinyl (in its two orientations) ligands are nearly perpendicular to the equatorial plane bisecting the angles N(1)—Co—N(4) and N(2)—Co—N(3). The Py ligand is always found to have such an orientation. The bond lengths and relevant coordination bond angles are given in Table 1. The Co—CH=CH₂ bond length of 1.966(6) Å compares with the values of 1.971(13) and 1.968(13) Å reported for (*p*-ClPh)₂C=C(Cl)Co(DH)₂Py [5], but is significantly, even if only slightly, shorter than those reported for methyl derivatives [1, 2, 3]. However, the Co—N(Py) distance of 2.073(3) Å falls within the range reported for other RCo(DH)₂Py compounds [1–4].

The known geometries of the R—Co—Py fragment in alkylcobaloximes are given in Table 2. Inspection of Table 2 shows that: (i) the Co—C distance in vinyl derivatives is slightly shorter (0.02 Å) than that in methyl derivatives, as expected on the basis of the different σ -covalent radii of C(*sp*²) and C(*sp*³). Thus no π -bonding contribution to the Co—C bond may be detected from the above

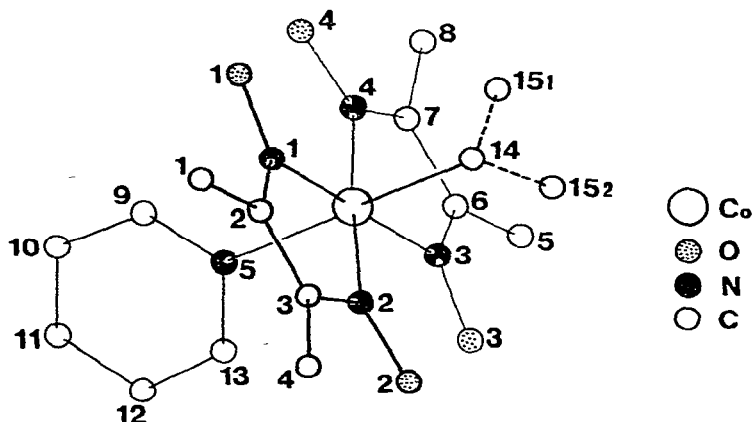


Fig. 1. A view of the molecule with the numbering scheme for its atoms.

TABLE 2

GEOMETRY OF THE R—Co—Py FRAGMENT IN ALKYLCOBALOXIMES

R	Co—C (Å)	Co—N (Å)	R—Co—Py (°)	Ref.
<i>(p</i> -ClPh) ₂ C=C(Cl)	1.971(13)	2.046(10)	179.2(4)	5
	1.968(13)	2.039(10)	176.7(4)	
H ₂ C=CH	1.966(6)	2.073(3)	178.1(2)	present work
Me	1.998(7)	2.068(3)	178.0(2)	1
MeOOCCH ₂	2.040(6)	2.040(6)	—	6
Me ₂ CH	2.085(3)	2.099(2)	175.4(1)	4

results. (ii) The *trans*-influence of a vinyl grouping, as measured by the lengthening of the CoN(Py) distance, is similar to that of an alkyl group. (iii) The C—Co—Py angle is affected by steric hindrance from the alkyl group as well as by the Co—C bond length [4].

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