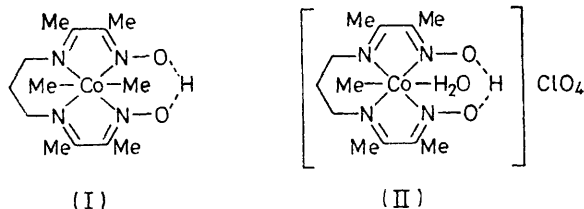


Crystal and Molecular Structure of Dimethyl-[3,3'-(trimethylenedinitrilo)-bis(butan-2-one oximato)]cobalt(III)

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The crystal and molecular structure of the title compound, (I), has been determined from three-dimensional *X*-ray data by conventional Fourier methods. Crystals are monoclinic with $a = 7.600(8)$, $b = 8.301(8)$, $c = 13.675(6)$ Å, $\beta = 113.5(3)^\circ$, $Z = 2$, space group *Pc*. The structure was refined by least-squares techniques to R 0.034 for 1342 independent reflexions. The co-ordination polyhedron of the cobalt atom is well represented as a distorted octahedron, the axial positions being occupied by two methyl groups [Co-C 2.045(8) and 2.049(8) Å] whereas the quadridentate {(doh)(do)pn} ligand occupies the four equatorial positions. The propylenediamine bridge has the expected *GG'* conformation [torsion angles around the C-C bonds: 62.9 and -67.6°]. Neglecting the central carbon atom of the propylene group, the equatorial ligand is nearly planar with two sets of Co-N distances [1.898(5) and 1.859(5) Å]. The values of the equatorial ligand bond lengths indicate π -electron delocalization in the five-membered rings. The *trans*-influence of methyl groups is discussed in relation to Co-C distances in the present and analogous compounds.

RECENTLY it has been shown¹⁻³ that methyl-cobalt chelates can act as methylating agents, their methyl-donor power depending on the nature of the chelating ligand and of the *trans* axial group. The last effect is evident from the marked increase in the methyl-donor power of dimethyl-[3,3'-(trimethylenedinitrilo)bis(butan-2-one oximato)]cobalt(III), (I), as compared with that of the monomethyl-aqua derivative (II). It has been suggested¹ that activation of one methyl group occurs through the very strong *trans*-effect of the other.



In order to establish the postulated¹ *trans*-dimethyl structure (I) and hence to study the *trans*-influence which methyl groups exert on each other, the crystal structure of (I) has been determined.

EXPERIMENTAL

Single orange crystals were obtained by slow evaporation of an aqueous acetone solution.⁴

Crystal Data.— $C_{13}H_{25}CoN_4O_2$, $M = 328.4$, Monoclinic, $a = 7.600(8)$, $b = 8.301(8)$, $c = 13.675(6)$ Å, $\beta = 113.5(3)^\circ$, $U = 791.0$ Å³, $Z = 2$, $D_c = 1.379$, $F(000) = 348$. Mo- $K\alpha$ radiation, $\lambda = 0.7107$ Å; μ (Mo- $K\alpha$) = 11.4 cm⁻¹. Space group *Pc* (C_2^2) or *P2/c* (C_{2h}^4) from absent reflexions: $h0l$ when l is odd; shown to be the former from structure determination.

Cell parameters, determined from Weissenberg photographs taken with Co- $K\alpha$ radiation ($\lambda = 1.7902$ Å), were refined with an on-line automated single-crystal Siemens diffractometer by use of Mo- $K\alpha$ radiation.

Intensity Measurements.—Intensity data were collected on a Siemens diffractometer by the θ - 2θ scan technique with the Mo- $K\alpha$ radiation for a maximum 2θ angle of 60° .

¹ G. Costa, G. Mestroni, and C. Cocevar, *Chem. Comm.*, 1971, 706.

² G. Costa, G. Mestroni, and C. Cocevar, *Tetrahedron Letters*, 1971, 21, 1869.

Reflexions with $I_0 < 3\sigma(I_0)$ were rejected, the remainder being corrected for Lorentz-polarization factors. A total of 1342 independent reflexions was obtained. No correction for absorption (μR ca. 0.09), extinction, or anomalous dispersion of the cobalt atom was applied.

Structure Determination and Refinement.—The structure was solved by the heavy-atom method, the approximate co-ordinates of the crystallographically independent cobalt atom being determined from a three-dimensional Patterson map.

The non-centrosymmetric space group was chosen since space group *P2/c* would require ($Z = 2$) the cobalt atom to lie on a two-fold axis or on a symmetry centre, thus entailing severe positional disorder of the structure. The choice of space group *Pc* has been confirmed by the successful refinement of the structure. After the isotropic block-diagonal least-squares refinement R was 0.062. Four cycles of anisotropic refinement reduced R to 0.041. At this stage of refinement, model inspection suggested that free rotation of the methyl groups should be sufficiently hindered to justify the attempt to locate their hydrogen atoms. In fact a difference-Fourier synthesis, calculated from reflexions with $(\sin \theta/\lambda) \leq 0.4$, allowed the unambiguous location of at least one hydrogen atom for each methyl group. The positions of the others were calculated assuming a regular geometry with C-H 1.09 Å. These positions were slightly corrected by rotation around the C-C bonds in order to minimize approximately the contributions of the methyl hydrogen atoms to the total conformational potential energy. The potential functions used for the H...H non-bonded interactions were those suggested by Giglio.⁵ Final anisotropic refinement reduced R to 0.034. The co-ordinates and thermal factors of the hydrogen atoms (set at 5 Å²) were held fixed. The function minimized was $\Sigma(w|F_o| - |F_c|)^2 / \Sigma w|F_o|^2$, where the weighting factor $w = (A + B|F_o| + C|F_o|^2)^{-1}$ with $A = 5.0$, $B = 1.0$, and $C = 0.0125$ was chosen so that $w(|F_o| - |F_c|)^2$ was nearly independent of both $|F_o|$ and $(\sin \theta/\lambda)$. Final atomic parameters are listed in Tables 1 and 2, together with their estimated standard deviations, calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares

³ G. Mestroni, C. Cocevar, and G. Costa, *Gazzetta*, 1973, 103, 273.

⁴ G. Costa, G. Mestroni, and G. Tauzher, *J.C.S. Dalton*, 1972, 450.

⁵ E. Giglio, *Nature*, 1969, 222, 339.

TABLE 1

Final co-ordinates ($\times 10^4$) of the atoms, with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Co	1008(2)	1321(1)	990(1)
O(1)	-2568(7)	2628(7)	-380(4)
O(2)	-2718(6)	-14(7)	400(4)
N(1)	-668(7)	2808(7)	49(4)
N(2)	2840(7)	2875(6)	978(4)
N(3)	2691(7)	-239(6)	1896(4)
N(4)	-817(7)	-180(6)	951(4)
C(1)	-1152(12)	5455(8)	-852(6)
C(2)	66(9)	4142(8)	-159(5)
C(3)	2143(9)	4147(7)	378(5)
C(4)	3326(13)	5492(9)	203(6)
C(5)	4950(10)	2689(10)	1597(7)
C(6)	5433(10)	1657(11)	2536(7)
C(7)	4789(10)	-82(9)	2324(7)
C(8)	2841(12)	-2302(10)	2803(6)
C(9)	1859(9)	-1496(7)	2089(5)
C(10)	-220(9)	-1456(8)	1548(5)
C(11)	-1547(11)	-2740(10)	1640(7)
C(12)	1231(10)	195(9)	-289(5)
C(13)	658(10)	2460(8)	2226(5)
H	-3050	1000	-20
1-H(1)	-2650	5164	-1088
2-H(1)	-814	5656	-1526
3-H(1)	-850	6574	-364
1-H(4)	2385	6391	-327
2-H(4)	4311	5043	-114
3-H(4)	4146	6079	979
1-H(5)	5566	2141	1067
2-H(5)	5589	3870	1832
1-H(6)	6974	1664	2988
2-H(6)	4748	2181	3037
1-H(7)	5287	-584	1752
2-H(7)	5392	-767	3065
1-H(8)	1798	-3789	2800
2-H(8)	3675	-2501	3608
3-H(8)	3828	-3479	2493
1-H(11)	-3044	-2416	1166
2-H(11)	-1386	-2836	2483
3-H(11)	-1244	-3897	1393
1-H(12)	2724	167	-177
2-H(12)	400	858	-1010
3-H(12)	684	-1020	-348
1-H(13)	-861	2682	2026
2-H(13)	1414	3608	2394
3-H(13)	1223	1714	2942

TABLE 2

Anisotropic temperature factors* ($\times 10^4$) of the non-hydrogen atoms, with their estimated standard deviations in parentheses

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Co	120(1)	-10(3)	42(1)	78(1)	-1(2)	33(0)
O(1)	157(9)	33(15)	6(9)	172(8)	33(9)	75(3)
O(2)	157(9)	-56(15)	24(9)	165(8)	7(10)	80(3)
N(1)	174(9)	48(14)	58(7)	124(7)	8(8)	41(2)
N(2)	169(8)	-46(14)	81(7)	116(7)	-4(8)	49(3)
N(3)	171(9)	15(14)	57(8)	92(6)	10(8)	54(3)
N(4)	167(9)	-27(14)	52(7)	107(7)	-13(8)	48(3)
C(1)	321(17)	104(21)	108(13)	103(9)	54(11)	77(4)
C(2)	218(11)	15(17)	76(8)	114(9)	19(8)	41(3)
C(3)	243(12)	-61(16)	105(8)	92(8)	-8(8)	47(3)
C(4)	390(20)	-120(22)	136(15)	98(10)	-7(12)	87(5)
C(5)	179(13)	-79(21)	80(13)	169(12)	17(15)	96(5)
C(6)	161(12)	-53(22)	18(13)	208(15)	27(14)	75(5)
C(7)	147(12)	27(20)	39(13)	127(10)	64(13)	109(6)
C(8)	296(17)	107(25)	88(13)	127(11)	83(12)	73(4)
C(9)	241(12)	37(17)	105(9)	91(8)	11(9)	54(3)
C(10)	233(11)	-38(19)	112(9)	115(9)	-10(10)	57(3)
C(11)	287(14)	-79(23)	192(12)	154(12)	27(14)	108(5)
C(12)	284(14)	-68(21)	121(10)	122(9)	-24(10)	58(3)
C(13)	263(13)	16(18)	118(9)	98(8)	-22(9)	53(3)

* The expression used is: $\exp[-(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)]$.

cycle. The numbering scheme of the atoms is shown in Figure 1 together with some mean values of bond lengths and angles for the two chemically equivalent halves of the

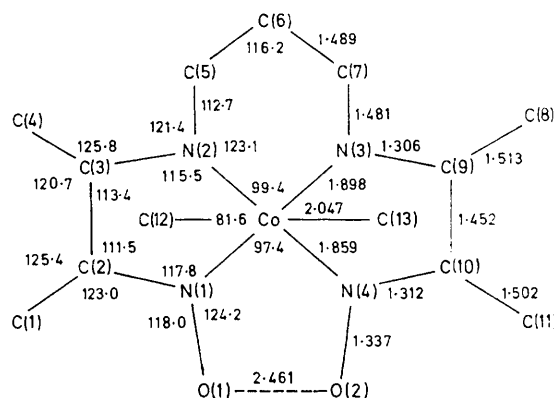


FIGURE 1 Numbering scheme of the atoms with mean values of bond lengths and angles

molecule. A full list of bond lengths and angles is reported in Table 3. Intra- and inter-molecular non-bonded distances ≤ 2.7 Å involving hydrogen atoms

TABLE 3

Bond lengths (Å) and angles ($^\circ$), with their estimated standard deviations in parentheses

(a) Distances			
Co-N(1)	1.869(5)	N(3)-C(7)	1.469(9)
Co-N(2)	1.903(6)	N(3)-C(9)	1.301(9)
Co-N(3)	1.893(5)	C(1)-C(2)	1.497(9)
Co-N(4)	1.849(6)	C(2)-C(3)	1.451(9)
Co-C(12)	2.049(8)	C(3)-C(4)	1.511(11)
Co-C(13)	2.045(8)	C(5)-C(6)	1.463(13)
O(1)-N(1)	1.332(7)	C(6)-C(7)	1.515(12)
O(2)-N(4)	1.343(6)	C(8)-C(9)	1.514(10)
N(1)-C(2)	1.321(9)	C(9)-C(10)	1.453(9)
N(2)-C(3)	1.312(7)	C(10)-C(11)	1.507(11)
N(2)-C(5)	1.493(8)		
(b) Angles			
N(1)-Co-N(2)	81.2(2)	Co-N(3)-C(7)	122.9(5)
N(1)-Co-N(3)	177.7(3)	Co-N(3)-C(9)	115.2(4)
N(1)-Co-N(4)	97.4(2)	C(7)-N(3)-C(9)	121.9(5)
N(1)-Co-C(12)	88.8(3)	Co-N(4)-O(2)	125.0(4)
N(1)-Co-C(13)	89.2(3)	Co-N(4)-C(10)	117.4(4)
N(2)-Co-N(3)	99.4(2)	O(2)-N(4)-C(10)	117.5(6)
N(2)-Co-N(4)	178.0(2)	N(1)-C(2)-C(1)	122.6(6)
N(2)-Co-C(12)	89.5(3)	N(1)-C(2)-C(3)	111.2(5)
N(2)-Co-C(13)	91.8(3)	C(1)-C(2)-C(3)	126.2(6)
N(3)-Co-N(4)	82.0(2)	N(2)-C(3)-C(2)	113.6(6)
N(3)-Co-C(12)	89.0(3)	N(2)-C(3)-C(4)	125.2(6)
N(3)-Co-C(13)	93.0(3)	C(2)-C(3)-C(4)	121.2(6)
N(4)-Co-C(12)	89.1(3)	N(2)-C(5)-C(6)	113.2(7)
N(4)-Co-C(13)	89.5(3)	C(5)-C(6)-C(7)	116.2(7)
C(12)-Co-C(13)	177.4(3)	N(3)-C(7)-C(6)	112.2(6)
Co-N(1)-O(1)	123.4(5)	N(3)-C(9)-C(8)	126.5(6)
Co-N(1)-C(2)	118.1(4)	N(3)-C(9)-C(10)	113.3(5)
O(1)-N(1)-C(2)	118.4(5)	C(8)-C(9)-C(10)	120.1(6)
Co-N(2)-C(3)	115.9(4)	N(4)-C(10)-C(9)	111.9(6)
Co-N(2)-C(5)	123.3(5)	N(4)-C(10)-C(11)	123.4(6)
C(3)-N(2)-C(5)	120.8(6)	C(9)-C(10)-C(11)	124.7(6)

are given in Table 4. Table 5 reports non-hydrogen intermolecular distances < 4 Å. Least-squares planes of interest are given in Table 6 together with the distances of the individual atoms from these planes. Observed and calculated structure factors are listed in Supplementary

TABLE 4

Intra- and inter-molecular non-bonded distances
 $\leq 2.70 \text{ \AA}$ involving hydrogen atoms

H...1-H(5 ^{VI})	2.34	1-H(6)...2-H(7)	2.37
1-H(1)...O(1)	2.31	1-H(6)...1-H(13 ^V)	2.62
1-H(1)...N(1)	2.58	2-H(6)...2-H(7)	2.49
2-H(1)...1-H(4)	2.41	2-H(6)...2-H(13)	2.61
2-H(1)...2-H(11 ^{IV})	2.65	2-H(6)...3-H(13)	2.66
2-H(1)...2-H(13 ^{III})	2.40	2-H(6)...N(2)	2.67
3-H(1)...1-H(4)	2.44	2-H(6)...N(3)	2.64
3-H(1)...3-H(11 ^I)	2.57	1-H(7)...1-H(12)	2.65
3-H(1)...3-H(12 ^I)	2.31	1-H(7)...N(3)	2.08
1-H(4)...3-H(12 ^I)	2.50	1-H(7)...1-H(11 ^V)	2.32
1-H(4)...3-H(13 ^{III})	2.68	2-H(7)...2-H(8)	2.26
2-H(4)...2-H(8 ^{IV})	2.66	2-H(7)...3-H(8)	2.52
3-H(4)...2-H(5)	2.22	2-H(7)...N(3)	2.08
3-H(4)...3-H(8 ^I)	2.21	1-H(8)...2-H(11)	2.42
3-H(4)...1-H(11 ^{VII})	2.40	1-H(8)...3-H(11)	2.35
1-H(5)...1-H(7)	2.49	1-H(8)...2-H(13 ^{II})	2.22
1-H(5)...1-H(12)	2.70	1-H(11)...O(2)	2.31
1-H(5)...N(2)	2.12	1-H(11)...N(4)	2.61
1-H(5)...1-H(13 ^V)	2.54	2-H(12)...N(1)	2.51
1-H(5)...O(2 ^V)	2.59	3-H(12)...N(4)	2.56
2-H(5)...1-H(6)	2.37	2-H(13)...N(2)	2.64
2-H(5)...2-H(6)	2.44	3-H(13)...N(3)	2.68
2-H(5)...N(2)	2.11		
1-H(6)...1-H(7)	2.50		

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z :

I $x, 1 + y, z$	VI $1 + x, y, z$
II $x, -1 + y, z$	VII $1 + x, 1 + y, z$
III $x, 1 - y, -\frac{1}{2} + z$	
IV $x, -y, -\frac{1}{2} + z$	

TABLE 5

Intermolecular distances (\AA) $< 4 \text{ \AA}$ involving non-hydrogen atoms, with estimated standard deviations in parentheses

C(1)...C(11 ^I)	3.84(1)	C(4)...C(11 ^{VII})	3.88(1)
C(1)...C(13 ^{III})	3.83(1)	C(11)...C(7 ^{VI})	3.95(1)
C(3)...C(8 ^I)	3.98(1)	C(12)...C(8 ^{IV})	3.99(1)
C(3)...C(8 ^{IV})	3.90(1)	C(12)...C(9 ^{IV})	3.95(1)
C(4)...C(8 ^I)	3.95(1)	C(12)...C(13 ^{IV})	3.93(1)
C(4)...C(8 ^{IV})	3.82(2)		

For definition of Roman numerals see footnote to Table 4.

TABLE 6

Equations of least-squares planes and, in square brackets, distances (\AA) of atoms from the planes. The equations are referred to the crystal axes and x, y, z are fractional co-ordinates

Plane (1): Co, O(1), O(2), N(1)—4, C(1)—5, C(7)—11
$-3.113x + 3.837y + 12.097z = 1.307$
[Co 0.022, O(1) -0.020, O(2) -0.044, N(1) -0.024, N(2) 0.034, N(3) -0.004, N(4) -0.033, C(1) 0.053, C(2) 0.008, C(3) 0.013, C(4) -0.051, C(5) 0.055, C(7) -0.079, C(8) 0.025, C(9) 0.006, C(10) 0.014, C(11) 0.046]
Plane (2): Co, N(2), N(3), C(5), C(7)
$-3.067x + 3.611y + 12.296z = 1.390$
[Co -0.005, N(2) -0.020, N(3) 0.030, C(5) 0.026, C(6) 0.660, C(7) -0.031]

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

⁶ F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

⁷ V. Albano, A. Domenicano, and A. Vaciano, *Gazzetta*, 1966, **96**, 922; A. Immirzi, *Ricerca sci.*, 1967, **10**, 846.

Publication No. SUP 21016 (5 pp; 1 microfiche).
 Atomic scattering factors were calculated according to ref. 6.

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 7. A local program was used to calculate the best molecular planes, whose equations were calculated according to ref. 8.

RESULTS AND DISCUSSION

The X-ray analysis results show that the complex has the suggested ¹ structure (I), the cobalt atom having a distorted octahedral co-ordination in which the methyl groups occupy the two axial positions (Figure 2). The

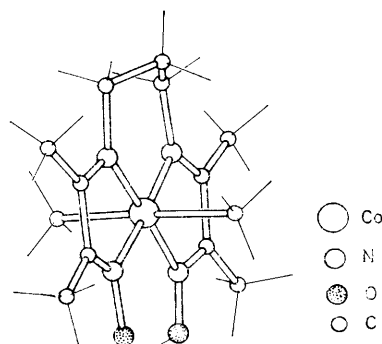


FIGURE 2 A sketch of the molecule as viewed along the b axis

four nitrogen atoms of the macrocyclic ligand occupy the equatorial positions and are almost exactly coplanar ($\pm 0.007 \text{ \AA}$). The cobalt atom is almost contained in this plane, being displaced only 0.029 \AA towards C(13). The six-membered ring has the expected flattened chair conformation, the Co, N(2), N(3), C(5), C(7) atoms being nearly coplanar ($\pm 0.03 \text{ \AA}$), whereas the torsion angles around the C(5)–C(6) and C(6)–C(7) bonds are 62.9° and -67.6° respectively.

Neglecting the C(6) atom, the whole equatorial ligand is nearly planar (Table 6). The two N–O distances [$1.332(7)$ and $1.343(6) \text{ \AA}$] are similar, which suggests⁹ a symmetric configuration of the hydrogen bridge in contrast with the fact that the bridging hydrogen atom is quite apparent on the difference electron-density map, being clearly located closer to the O(2) oxygen atom. The O(2)–H and O(1)–H distances are 0.99 and 1.53 \AA respectively with N(4)–O(2) \cdots H and O(2)–H \cdots O(1) bond angles of 112.3° and 153.5° . The O(1) \cdots O(2) distance is $2.461(8) \text{ \AA}$. The mean of the four C–CH₃ bond lengths [$1.506(2) \text{ \AA}$] is in good agreement with the expected value.¹⁰ The mean values of the N–O, N–C, and C–C bond lengths [$1.338(4)$, $1.309(2)$, and $1.452(1) \text{ \AA}$] indicate extended conjugation in the two five-membered rings. In fact, the bond orders cal-

⁸ V. Schomaker, J. Waser, R. F. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

⁹ K. Bowman, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, 1972, **94**, 727.

¹⁰ *Chem. Soc. Special Publ.*, No. 13, 1965.

culated according to Bernstein's equation¹¹ for the N-O, N-C, and C-C bonds are 1.43, 1.63, and 1.18, in agreement with a π -electron delocalization. The values assumed for the single-bond covalent radii are 0.70, 0.75, and 0.74 Å for N(sp^2), C(sp^2), and O. The data available so far for bis(dimethylglyoximate)-complexes (dmg) indicate that such delocalization is far less extended.^{9,12-15}

There are pairs of similar Co-N bond lengths, the longer being those involving the nitrogen atoms of the propylenedi-imine bridge: 1.903(6) and 1.893(5) Å vs. 1.869(5) and 1.849(6) Å for the nitrogen atoms of the N-O groups. Similar values were found for the analogous methyl-aqua derivative (II) [mean 1.93(3) and 1.87(3) Å].¹⁶ However, in the Co^{III} (dmg) complexes^{13,14} the four Co-N bond lengths are equivalent, mean 1.884(1) Å. Thus the observed difference in the Co-N distances may be due to their different nature and to a different π -contribution.

The two axial Co-C distances are equal [Co-C(12) 2.049(8), Co-C(13) 2.045(8) Å]. The mean value (2.047 Å) is quite close to those in other octahedral complexes with quadridentate nitrogen ligands such as the *O*-methylcarboxymethyl-bis(dimethylglyoximate)pyridinatecobalt(III) [2.040(6) Å] and the Vitamin B₁₂ coenzyme [2.05 Å].¹³ On the other hand the value appears longer than that found in (II) of 1.99(4) Å. However the difference may be not significant in view of the low accuracy of the latter structure determination. In any case, such data indicate that the Co-C distances are not particularly long in the dimethyl derivative as would be expected if one methyl group exerted a strong *trans*-influence on the other. Therefore, in this case, no information can be derived from a ground-state property, such as distances, about the

reactivity of such a compound. A similar constancy of Co-C distance has already been found in a series of other octahedral cobalt(III) complexes with quadridentate Schiff bases.¹⁷ This result is not in fact unexpected since it has been found that *trans*-influence effects are determined by the relative σ -donor properties of the 'influencing' and 'influenced' ligands.¹⁸ In more quantitative terms the *trans*-influence of a ligand may be related to the $S^2/\Delta E$ ratio, where S is the overlap integral of the interacting metal-ligand σ orbitals and ΔE their absolute energy separation.¹⁸ The Co-C bond length would therefore only be expected to be lengthened by ligands which are able to form σ bonds stronger than do C(sp^3)-ligands. Thus we may assume that, in the absence of significant distortion of the whole molecule, the value of 2.047 Å can be taken as that to be expected for a σ Co^{III}-C(sp^3) bond length with quadridentate ligands of the dmg type.

The value of 2.047 Å is significantly greater than that found in other octahedral organocobalt(III) complexes containing as equatorial ligands quadridentate Schiff bases such as salen [bis(salicylaldehyde)ethylenediimine dianion] or bae [bis(acetylaceton)ethylenediimine dianion] in which the mean values are 2.00(1) and 1.95(1) Å.¹⁶ This result confirms the existence of a *cis*-influence exerted by the equatorial ligands on the Co-C bonds. The decrease of the Co-C bond lengths between (I) and (II) and complexes with dmg ligands, and those with salen or bae is probably related to the different nature of the in-plane donor atoms and to the differing extent of conjugation which should also involve the cobalt atom.¹⁹

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