Steric Effects in the Reversible Oxygenation of Cobalt–Schiff-base Complexes. Part II.[1] Crystal and Molecular Structure of [*NN'*-Butylenebis(salicylideneiminato)]pyridinecobalt(II)

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray data by Fourier methods and refined by anisotropic block-diagonal least squares to *R* 0·058 for 3230 independent reflections. Crystals are monoclinic, space group $P2_1$, with cell parameters a = 18·128, b = 10·597, c = 11·381 Å, and β = 100·6°, Z = 4. The two crystallographically independent molecules (A) and (B) are stereochemically non-equivalent: in (A) the cobalt atom geometry is a square pyramid with the metal atom displaced 0·21 Å towards the apical pyridine, whereas in (B) it is largely distorted towards a trigonal bipyramid. There are significant differences in the co-ordination bond lengths involving the quadridentate ligand: mean Co–O 1·905(8) in (A) and 1·939(7) Å in (B), Co–N 2·140(7) and 2·056(8) (B), and 1·887(9) Å (A). However in both molecules the butylene-bridge methyl groups are found in the bis-axial conformation, in spite of steric hindrance due to pyridine. The behaviour towards oxygenation is discussed on the basis of the structural results.

RECENT investigations[2] have shown that the ethylene-bridge substituted compounds of the well known synthetic oxygen carrier *NN'*-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), exhibit a different behaviour towards oxygen absorption in σ-donor solvents, mainly due to the configuration of the substituted bridge.

For example[3] the *meso* form of *NN'*-butylenebis(salicylideneiminato)cobalt(II), [Co{salbn(*m*)}], shows a significantly larger value of the equilibrium constant than the corresponding optically active form Co{salbn(+)} for reaction (1).

$$\text{Co(chel)} + \text{O}_2 + \text{Lewis base} \longrightarrow \text{(Lewis base)Co(chel)(O}_2\text{)} \quad (1)$$

The existence of steric effects in the reversible oxygenation of these compounds is clearly related to conformational features. Therefore the elucidation of the molecular structure of such compounds and of their pyridine addition complexes in the solid state can give useful information on the problem. We have already reported[1] the crystal and molecular structure of the four-co-ordinate [Co{salbn(m)}] and [Co{salbn(+)}] complexes. We report here the crystal and molecular structure of the monopyridine addition complex of Co-

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[1] Part I, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1973, 419.

[2] C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J.C.S. Dalton*, 1973, 754 and refs. therein.

[3] R. Ugo, A. Fusi, A. Pasini, M. Gullotti, and E. Cesarotti, Abstracts Ann. Meeting Inorg. Chem., Taormina, 1972, p. A6.

{salbn(+)}, [Co{salbn(+)}(py)]. A preliminary report has been made.[4]

EXPERIMENTAL

Crystal Data.—$C_{23}H_{23}CoN_3O_2$, $M = 432{\cdot}2$, Monoclinic, $a = 18{\cdot}128$, $b = 10{\cdot}597$, $c = 11{\cdot}381$ Å, $\beta = 100{\cdot}6°$, $U = 2149{\cdot}1$ Å^3, D_m (by flotation) $= 1{\cdot}37$ g/cm^3, $Z = 4$, $D_c = 1{\cdot}34$ g/cm^3. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-$K\alpha$) $= 8{\cdot}6$ cm^{-1}. Space group $P2_1$ (C_2^2). Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with an on-line automated single-crystal Siemens diffractometer (Mo-K_α).

Intensity Measurements.—Three-dimensional intensity data were collected on the Siemens diffractometer by the θ—2θ scan technique and Mo-K_α radiation for a maximum 2θ angle of 60°. The crystal used, of dimensions $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}4$ mm, was enclosed under nitrogen in a thin-walled capillary, since the crystals easily lose pyridine when exposed to air. All reflections having $I_o < 3\sigma(I_o)$ were rejected, the remainder being corrected for Lorentz-polarization factors. A total of 3230 independent reflections was used in the subsequent calculations. No correction for absorption ($\mu\,.\,\rho$ *ca.* 0·25) or anomalous dispersion of the cobalt atom was applied.

During data collection, the intensities of the two reference reflections decreased with time; this intensity decrease could be well represented by a simple dependence of I_n/I_o as a function of n (the number of the reflection in this order of collection), where I_n was the actual intensity measured at n and I_o the starting intensity of each reference reflection.

The relationships were:

$$I_n/I_o = 1{\cdot}00 - 3{\cdot}33 \times 10^{-5}\,.\,n \; (1 \leqslant n \leqslant 3600)$$

$$I_n/I_o = 0{\cdot}88 - 6{\cdot}66 \times 10^{-5}\,.\,n \; (3600 < n)$$

It was observed that the falling off of the intensity was independent of the Bragg angle.

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods. After a least-squares isotropic refinement R was 0·075. After three cycles of anisotropic block-diagonal refinement a three-dimensional difference-Fourier synthesis was calculated to locate the hydrogen atoms. Calculated positions of these all occurred in regions of positive electron density. However the two methyl groups of one molecule appeared clearly disordered and their hydrogen atoms were therefore not located and their contributions to the structure factors was not included. Final anisotropic block-diagonal least-squares refinement gave R 0·058. The co-ordinates and the temperature factors of the hydrogen atoms (set at B 5 Å^2) were not allowed to vary. The final weighting scheme was $w = 1/(A + B\,|F_o| + C\,|F_o|^2)$, where $A = 8{\cdot}0$, $B = 1{\cdot}0$, and $C = 0{\cdot}009$, chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and (sin θ/λ). Final atomic parameters are listed in Tables 1 and 2, together with their estimated standard deviations. The numbering scheme for the atoms is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20884 (15 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 5.

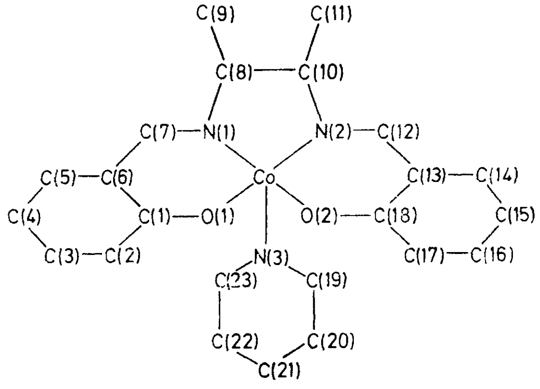

FIGURE 1 Numbering scheme for the atoms of both the crystallographically independent molecules

TABLE 1

(*a*) Fractional co-ordinates (× 10^4) and anisotropic factors* (× 10^5) for molecule (A), with estimated standard deviations in parentheses

	x	y	z	B/Å^2
Co	3932(1)	4100(1)	−513(1)	*
O(1)	3374(4)	2622(7)	−289(5)	*
O(2)	4066(3)	3379(7)	−1992(6)	*
N(1)	3949(5)	4672(9)	1062(8)	*
N(2)	4689(5)	5270(8)	−523(7)	*
N(3)	2970(4)	5175(9)	−1299(7)	*
C(1)	3148(5)	2251(5)	689(8)	3·50(16)
C(2)	2792(6)	1102(12)	672(10)	5·02(22)
C(3)	2504(7)	683(13)	1679(11)	5·63(24)
C(4)	2639(7)	1358(14)	2739(11)	5·74(26)
C(5)	3002(6)	2509(12)	2797(10)	4·72(21)
C(6)	3254(5)	2989(11)	1754(9)	4·20(18)
C(7)	3676(6)	4135(14)	1906(10)	5·37(22)
C(8)	4365(8)	5870(15)	1324(13)	6·97(32)
C(9)	3867(9)	7011(19)	925(16)	8·72(42)
C(10)	4987(9)	5826(17)	703(14)	7·84(36)
C(11)	5644(9)	4971(22)	1362(15)	9·13(40)
C(12)	5077(7)	5507(13)	−1393(11)	5·31(23)
C(13)	4916(6)	4911(13)	−2533(9)	4·84(19)
C(14)	5348(7)	5341(13)	−3402(11)	5·94(27)
C(15)	5288(7)	4731(14)	−4453(11)	6·24(27)
C(16)	4795(7)	3657(13)	−4726(11)	5·77(25)
C(17)	4399(6)	3222(11)	−3883(9)	4·47(20)
C(18)	4449(4)	3829(9)	−2747(7)	3·40(16)
C(19)	2952(7)	5893(13)	−2276(11)	5·78(25)
C(20)	2353(9)	6671(18)	−2731(14)	7·89(36)
C(21)	1757(9)	6704(18)	−2193(14)	7·67(36)
C(22)	1731(8)	5927(17)	−1238(14)	7·64(35)
C(23)	2334(7)	5190(14)	−844(11)	6·10(26)

* Anisotropic temperature factor in the form: $\exp - (h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})$, with parameters

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	289(3)	−220(17)	191(9)	763(11)	−54(19)	679(8)
O(1)	427(21)	−349(65)	340(51)	824(66)	120(97)	650(46)
O(2)	329(19)	−321(63)	260(52)	838(64)	−181(105)	891(53)
N(1)	460(30)	−292(93)	261(76)	1185(109)	−624(145)	931(70)
N(2)	432(28)	−450(81)	199(73)	920(97)	−223(135)	968(70)
N(3)	386(26)	−47(86)	129(68)	880(83)	76(136)	847(63)

(*b*) Co-ordinates of hydrogen atoms, numbered according to the atom to which they are bonded

	x	y	z		x	y	z
H(2)	2716	533	−112	H(15)	5624	5029	−5102
H(3)	2178	−193	1607	H(16)	4740	3188	−5589
H(4)	2438	1009	3503	H(17)	4036	2404	−4102
H(5)	3105	3031	3611	H(19)	3455	5913	−2696
H(7)	3733	4663	2765	H(20)	2399	7256	−3511
H(8)	4551	5895	2297	H(21)	1269	7287	−2542
H(10)	5249	6748	623	H(22)	1239	5921	−795
H(12)	5550	6161	−1200	H(23)	2314	4584	− 56
H(14)	5724	6165	−3145				

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, index issue.

[4] M. Calligaris, G. Nardin, and L. Randaccio, Abstracts Italo-Yugoslav Meeting Crystallography, Trieste, 1973, p. 202.

[5] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 6. A local program was used to obtain best molecular planes, whose equations were calculated according to ref. 7.

TABLE 2

(a) Fractional co-ordinates ($\times 10^4$) and anisotropic temperature factors * ($\times 10^5$) for molecule (B) with estimated standard deviations in parentheses

	x	*y*	*z*	$B/Å^2$
Co	279(1)	4985(1)	3159(1)	*
O(1)	967(3)	6374(7)	3195(6)	*
O(2)	−699(3)	5766(6)	2605(5)	*
N(1)	1211(4)	3901(7)	4054(6)	*
N(2)	−191(4)	3938(8)	4353(6)	*
N(3)	286(4)	4096(8)	1478(6)	*
C(1)	1716(4)	6433(9)	3488(7)	3·15(15)
C(2)	2084(5)	7515(10)	3205(8)	3·91(17)
C(3)	2857(6)	7680(12)	3541(10)	4·89(22)
C(4)	3288(6)	6750(12)	4149(10)	5·00(22)
C(5)	2963(5)	5684(11)	4437(9)	4·24(18)
C(6)	2168(5)	5461(9)	4106(8)	3·36(15)
C(7)	1883(5)	4298(10)	4437(8)	3·75(16)
C(8)	943(5)	2733(10)	4538(8)	3·85(17)
C(9)	687(6)	1792(11)	3591(9)	4·42(20)
C(10)	325(5)	3151(10)	5210(9)	4·05(18)
C(11)	622(6)	3899(13)	6332(10)	5·33(22)
C(12)	−880(4)	3999(10)	4531(7)	3·37(15)
C(13)	−1462(4)	4808(8)	3892(7)	2·95(13)
C(14)	−2156(5)	4789(10)	4268(8)	3·78(16)
C(15)	−2737(5)	5572(11)	3787(9)	4·42(19)
C(16)	−2632(5)	6367(10)	2868(8)	3·92(17)
C(17)	−1954(5)	6427(9)	2481(8)	3·20(15)
C(18)	−1343(4)	5647(8)	2968(7)	2·70(13)
C(19)	−348(6)	3947(12)	701(9)	5·11(21)
C(20)	−371(8)	3239(16)	−323(13)	6·94(32)
C(21)	249(7)	2785(14)	−635(11)	6·24(28)
C(22)	888(7)	2926(14)	135(12)	6·40(28)
C(23)	888(6)	3630(11)	1188(9)	4·63(20)

* Anisotropic temperature factors (see Table 1), with parameters:

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	225(2)	57(11)	162(7)	566(9)	130(17)	522(6)
O(1)	297(19)	112(61)	218(54)	729(64)	245(105)	964(56)
O(2)	244(15)	115(56)	299(43)	859(61)	600(89)	703(43)
N(1)	331(21)	50(71)	187(57)	552(69)	97(111)	735(54)
N(2)	285(19)	231(71)	342(51)	870(73)	712(114)	728(52)
N(3)	306(20)	50(76)	142(52)	809(71)	292(114)	516(47)

(*b*) Hydrogen atom co-ordinates for molecule (B)

	x	*y*	*z*		*x*	*y*	*z*
H(2)	1744	8273	2712	H(21)	206	2308	−1509
H(3)	3116	8535	3293	H(22)	1388	2463	−57
H(4)	3882	6947	4400	H(23)	1427	3827	1746
H(5)	3304	4967	4901	H(8)	1417	2339	5169
H(7)	2260	3716	5074	1-H(9)	1156	1529	3148
H(12)	−1039	3376	5190	2-H(9)	244	2171	2942
H(14)	−2239	4112	4945	3-H(9)	502	949	3988
H(15)	−3264	5600	4139	H(10)	15	2320	5440
H(16)	−3099	6952	2433	1-H(11)	160	4162	6785
H(17)	−1911	7098	1771	2-H(11)	893	4742	6108
H(19)	−869	4354	900	3-H(11)	1016	3333	6945
H(20)	−915	3090	−886				

RESULTS AND DISCUSSION

The Structure.—The two crystallographically independent molecules are shown in Figure 2. The co-ordination polyhedron around the cobalt atom of molecule (A) may be described as a distorted square pyramid with the metal atom displaced 0·206 Å towards the pyridine molecule. On the contrary, the geometry in molecule (B) is intermediate between a square pyramid and a trigonal bipyramid. The test suggested by Zemann[8] to distinguish the above two geometries, on the basis of the *R* factor, $\Sigma|X\widehat{M}X_{exp} - X\widehat{M}X_{theor}|/\Sigma X\widehat{M}X_{theor.}$, for the ten ligand–metal–ligand angles, may be indicative. In molecule (A) *R* was 0·07 for a square pyramid, but 0·11 and 0·16 for the two possible bipyramidal arrangements. In molecule (B), *R* was 0·08 for a square pyramid, against 0·08 and 0·20 for a trigonal bipyramid with O(2), N(1), and O(1), N(2) respectively as axial ligands. The geometry of molecule (A) is therefore close to the square pyramid with the metal atom above the basal plane, whereas in molecule (B) it is clearly intermediate between the two limiting geometries.

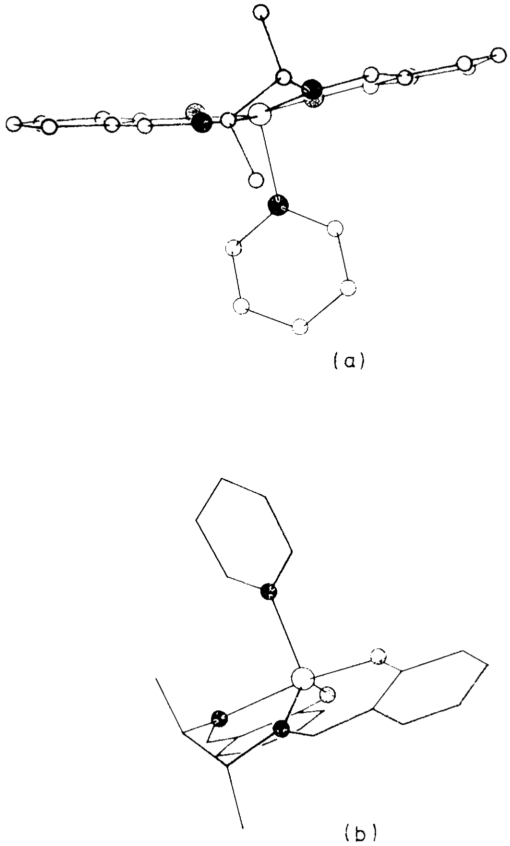

FIGURE 2 (a) Molecule (A) and (b) molecule (B)

The different co-ordination found in the two molecules corresponds to a marked difference in the co-ordination bond lengths. The Co–N distances involving the salbn(+) ligand in molecule (A) are *ca.* 0·20 Å shorter than the corresponding distances for the bipyramid, as already found in other five-co-ordinate complexes of cobalt.[9] However, the Co–N(py) bond lengths do have the same value in both molecules. A similar but far

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[6] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922; A. Immirzi, *Ricerca sci.*, 1967, **10**, 846.

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

[8] Zemann, *Z. anorg. Chem.*, 1963, **324**, 341.

[9] L. Sacconi, *Co-ordination Chem. Rev.*, 1972, **8**, 351.

less marked shortening (0·02 Å) is observed for the Co–O bond lengths. Bond lengths and angles (Table **3**) in the equatorial ligand in both molecules are comparable with those already found in similar complexes.[10]

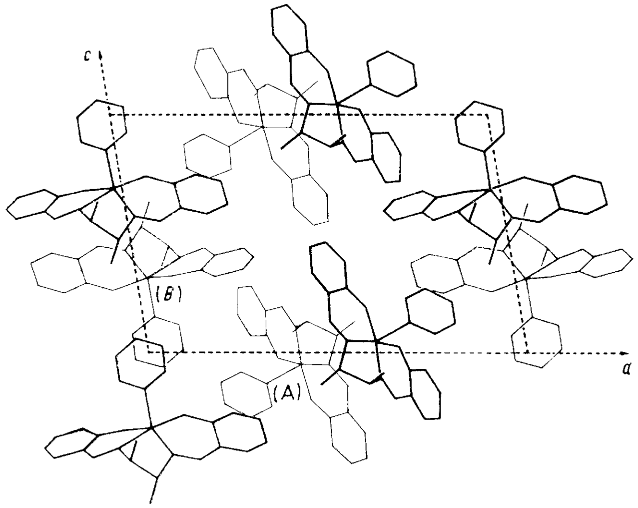

FIGURE 3 A projection of the crystal structure along the *b* axis, in a left-handed system of axes

Intermolecular contacts are quite normal, the molecules being loosely held together in pairs by van der Waals forces (Figure **3**).

TABLE 3

Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses for molecules (A) and (B)

(*a*) Distances

	Molecule (A)	Molecule (B)
Co–O(1)	1·907(8)	1·925(7)
Co–O(2)	1·904(7)	1·953(6)
Co–N(1)	1·887(9)	2·140(7)
Co–N(2)	1·851(9)	2·056(8)
Co–N(3)	2·137(8)	2·135(7)
O(1)–C(1)	1·315(12)	1·339(9)
O(2)–C(18)	1·291(11)	1·314(10)
N(1)–C(7)	1·291(16)	1·287(11)
N(1)–C(8)	1·479(18)	1·473(13)
N(2)–C(10)	1·519(17)	1·479(12)
N(2)–C(12)	1·339(16)	1·303(11)
N(3)–C(19)	1·343(16)	1·324(12)
N(3)–C(23)	1·348(16)	1·295(14)
C(1)–C(2)	1·377(16)	1·394(14)
C(1)–C(6)	1·426(14)	1·420(12)
C(2)–C(3)	1·415(18)	1·394(14)
C(3)–C(4)	1·385(18)	1·364(16)
C(4)–C(5)	1·382(19)	1·342(17)
C(5)–C(6)	1·441(16)	1·441(13)
C(6)–C(7)	1·429(18)	1·414(14)
C(8)–C(9)	1·527(24)	1·479(14)
C(8)–C(10)	1·437(24)	1·533(14)
C(10)–C(11)	1·573(24)	1·515(15)
C(12)–C(13)	1·424(17)	1·447(11)
C(13)–C(14)	1·444(18)	1·401(12)
C(13)–C(18)	1·419(15)	1·424(12)
C(14)–C(15)	1·346(18)	1·373(13)
C(15)–C(16)	1·445(19)	1·383(15)
C(16)–C(17)	1·379(18)	1·381(14)
C(17)–C(18)	1·432(13)	1·411(12)
C(19)–C(20)	1·386(21)	1·380(19)
C(20)–C(21)	1·337(25)	1·329(21)
C(21)–C(22)	1·371(24)	1·326(17)
C(22)–C(23)	1·351(20)	1·412(18)

TABLE 3 (*Continued*)

(*b*) Angles

	Molecule (A)	Molecule (B)
Co–O(1)–C(1)	127·9(6)	131·7(6)
Co–O(2)–C(18)	127·7(6)	131·6(5)
Co–N(1)–C(7)	128·6(7)	127·0(7)
Co–N(1)–C(8)	112·7(8)	110·1(5)
Co–N(2)–C(10)	113·1(8)	116·8(6)
Co–N(2)–C(12)	128·4(8)	127·0(6)
Co–N(3)–C(19)	122·9(7)	120·2(7)
Co–N(3)–C(23)	122·4(8)	122·8(6)
O(1)–Co–O(2)	86·9(3)	103·2(3)
O(1)–Co–N(1)	93·1(4)	87·1(3)
O(1)–Co–N(2)	164·4(3)	138·1(3)
O(1)–Co–N(3)	94·7(3)	104·1(3)
O(1)–C(1)–C(2)	118·1(9)	119·2(8)
O(1)–C(1)–C(6)	122·8(9)	123·8(8)
O(2)–Co–N(1)	170·4(3)	166·3(3)
O(2)–Co–N(2)	92·8(3)	88·9(3)
O(2)–Co–N(3)	94·1(3)	93·0(3)
O(2)–C(18)–C(13)	124·1(8)	123·8(7)
O(2)–C(18)–C(17)	118·8(8)	119·9(8)
N(1)–Co–N(2)	84·7(4)	77·4(3)
N(1)–Co–N(3)	95·5(4)	93·2(3)
N(1)–C(7)–C(6)	123·7(11)	124·6(8)
N(1)–C(8)–C(9)	111·6(11)	112·0(8)
N(1)–C(8)–C(10)	106·9(13)	105·4(8)
N(2)–Co–N(3)	100·9(4)	115·2(3)
N(2)–C(10)–C(8)	106·6(12)	105·4(8)
N(2)–C(10)–C(11)	108·9(13)	110·2(9)
N(2)–C(12)–C(13)	122·9(11)	125·6(8)
N(3)–C(19)–C(20)	123·0(13)	121·1(11)
N(3)–C(23)–C(22)	125·2(13)	123·3(9)
C(1)–C(2)–C(3)	120·5(11)	122·7(9)
C(1)–C(6)–C(5)	119·6(10)	118·0(9)
C(1)–C(6)–C(7)	123·7(10)	124·0(8)
C(2)–C(1)–C(6)	119·1(10)	117·0(7)
C(2)–C(3)–C(4)	120·7(12)	120·1(11)
C(3)–C(4)–C(5)	120·3(12)	119·7(10)
C(4)–C(5)–C(6)	119·5(11)	122·5(9)
C(5)–C(6)–C(7)	116·4(10)	118·1(8)
C(7)–N(1)–C(8)	118·7(11)	120·3(7)
C(8)–C(10)–C(11)	112·2(14)	113·1(8)
C(9)–C(8)–C(10)	110·7(14)	113·5(8)
C(10)–N(2)–C(12)	117·4(10)	115·7(8)
C(12)–C(13)–C(14)	116·0(11)	116·8(8)
C(12)–C(13)–C(18)	122·0(11)	123·0(7)
C(13)–C(14)–C(15)	119·5(12)	122·4(9)
C(13)–C(18)–C(17)	117·0(9)	116·2(7)
C(14)–C(13)–C(18)	121·3(10)	120·0(7)
C(14)–C(15)–C(16)	121·0(13)	117·9(9)
C(15)–C(16)–C(17)	119·6(11)	121·6(9)
C(16)–C(17)–C(18)	121·6(11)	121·9(9)
C(19)–N(3)–C(23)	114·8(10)	116·9(9)
C(19)–C(20)–C(21)	119·2(16)	121·8(12)
C(20)–C(21)–C(22)	119·7(16)	117·5(13)
C(21)–C(22)–C(23)	117·8(15)	119·0(12)

Conformational Aspects.—The two halves of the quadridentate ligand of molecule (A) are planar (±0·080 Å) making an angle of 11·2° assuming an asymmetric umbrella shape[10] the angles with the co-ordination plane O(1), O(2), N(1), N(2) being 2·8 and 10·6° respectively. A slight twisting of the two halves of the equatorial ligand is observed however, the four donor atoms being displaced ±0·05 Å from their mean plane.* In molecule (B) the two moieties make an angle of 143·9° not far from the value of the angle O(1)–Co–N(2) of 138·1°.

The methyl groups of the butylene bridge are bis-axial with a pseudo-*trans*-conformation in both molecules, the

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* Deviations (Å) of atoms from the co-ordination plane are: O(1) −0·047, O(2) 0·048, N(1) 0·049, N(2) −0·050, Co 0·206.

[10] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 543.

torsion angles being 161·0 [molecule (A)] and 168·2° [molecule (B)]. The two nitrogen atoms of the bridge are in a nearly *gauche* conformation with torsion angles of 41·9° in molecule (A) and 51·5° in the molecule (B).

In spite of the different arrangement of the donor atoms around the cobalt atom the four butylene carbon atoms are nearly equidistant from the pyridine plane in both molecules. The two methyl groups prefer the bis-axial conformation in spite of the steric hindrance of the pyridine molecule. This situation is at odds with that in octahedral complexes with substituted ethylenediamine chelates.[11] On the basis of the present results the difference may be mainly attributed to the different nature (trigonal or tetrahedral) of the nitrogen atoms. Furthermore the stability of the methyl bis-axial conformation with respect to the bis-equatorial one, in which significant angle strains are involved, may explain the existence of two different stereochemistries in the same compound. Thus, as rotation of the pyridine molecule occurs around the Co–N bond, the steric repulsion with the butylene bridge is alleviated by interconversion of the square pyramidal and bipyramidal geometries. Rotation of the pyridine molecule seems likely because of thermal and entropic effects in solution as well as packing effects in the solid state.

Oxygen Uptake.—The equilibrium constants of reaction (1) in dimethylformamide for the *meso*-forms of Co(salbn) or Co(salstien) * are *ca.* 10 times larger that those of the corresponding optically active forms.[3] On the contrary no appreciable difference has been found among the Co(salchx) forms. The bis-axial and -equatorial conformations are, in principle, both possible for the optically active forms and their five-co-ordinate pyridine addition complexes, whereas for Co(salchx) only the bis-equatorial conformation is possible because of the necessity of closing the cyclohexane ring. In the four-co-ordinate Co{salbn(+)} compound the bis-axial conformation was found to be the most stable in the solid state and we suggested that such a conformation should again be the most stable in the five-co-ordinate pyridine addition complex on the basis of a simple conformational calculation,[1] as has actually been found. However, the influence of the ethylene-bridge substituents was suggested to act through a destabilization of the pyridine–cobalt bond [3,12] or, alternatively, through their steric hindrance to the attack by oxygen of the cobalt atom. On the contrary, the lack of such influence in the Co(salchx) complexes could explain their different behaviour.

The present structural results confirm the bis-axial conformation in the five-co-ordinate complex. However they do not support the first hypothesis because no lengthening of the Co–N distance [2·136(8) Å] is found as compared with that [13] [2·10(2) Å] in the much less hindered Co(salen)(py) complex. Furthermore the axial groups should not influence the oxygen uptake through direct steric interaction with oxygen, but rather through an interaction with the apical ligand which provokes a change in the co-ordination around the cobalt atom (see previous section). In fact a square-pyramidal geometry may be assumed to represent a ' better situation ' for the absorption than the bipyramidal one, in which the cobalt atom is much more screened by ligands from the attack of a sixth group.

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* Co(salstien) is *NN'*-stilbenebis(salicylideneiminato)cobalt(II), Co(salchx) is *NN*-'cyclohexylenebis (salicylideneiminato)cobalt(II).

[11] R. D. Gillard and H. M. Irving, *Chem. Rev.*, 1965, **65**, 603.

[12] M. Calligaris, G. Nardin, and L. Randaccio, ref. 3, p. B14.

[13] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc. (A)*, 1970, 2411.