Crystal and Molecular Structure of the Reversible Dioxygen Adduct of [*NN'*-4-Methyl-4-azaheptane-1,7-diylbis(salicylideneiminato)]cobalt(II) †

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The crystal and molecular structure of the title complex, $[\{Co(salmhpn)\}_2]\cdot O_2\cdot 2C_6H_6$, has been determined from *X*-ray data collected by counter techniques. The compound crystallizes from benzene in space group $P\bar{1}$ with cell parameters (at 293 K) a = 17.045(4), b = 12.697(3), c = 11.668(3) Å, α = 94.23(3), β = 90.06(3), γ = 100.43(3)°, and Z = 2. The structure has been refined to R = 0.087 and R' = 0.093 on the basis of 1 482 independent reflections. The crystal lattice contains both dioxygenated and non-dioxygenated molecules, in 1 : 1 ratio, in which the cobalt atoms are octahedral and five-co-ordinate respectively. In the dioxygenated molecules, the five-co-ordinating positions of the low-spin cobalt atoms are occupied by the donor atoms of the quinquedentate ligand salmhpn and the sixth position by a dioxygen molecule bound in a bent end-on fashion. The co-ordinated dioxygen molecule shows a two-fold statistical disorder and the interatomic O–O distances average 1.06(5) Å. The non-dioxygenated molecules, containing high-spin cobalt(II) atoms, do not show any appreciable interaction with the dioxygenated moieties. The shortest cobalt–cobalt distance is 7.54 Å. The crystal packing shows benzene molecules close to the co-ordinated dioxygen molecules.

The study of the conformational changes accompanying the co-ordination of dioxygen to metal complexes can be of great help in understanding the structural changes which occur at the heme centre in hemoglobin and myoglobin upon the binding of dioxygen. In particular for hemoglobin, current interpretations of its co-operative binding mechanism are based upon the subtle changes occurring in the iron stereochemistry.[1]

Unfortunately investigations of this kind are not numerous because of the difficulties of obtaining single crystals suitable for *X*-ray diffraction of both the precursor and the dioxygen adduct.[2-6]

We have recently reported the salient features of the structure of the reversible dioxygen adduct of the title compound, $[\{Co(salmhpn)\}_2]\cdot O_2\cdot 2C_6H_6$, which showed the unusual presence of both dioxygenated and non-dioxygenated complex molecules.[7] In the attempt to isolate crystals of the precursor complex for *X*-ray analysis, three different crystalline forms of [Co(salmhpn)] were obtained: two from benzene [orthorhombic (β) and monoclinic (γ)], both crystallizing with one solvent molecule per complex molecule, and one from acetone (α). Although all these modifications dissolved in benzene, and adsorb oxygen reversibly, only one form from benzene is reactive towards oxygen in the solid state. The structures of the three precursor forms recently reported show essentially the same stereochemistry about the cobalt atom.[8,9] We wish to report here the details of the structure of $[\{Co(salmhpn)\}_2]\cdot O_2\cdot 2C_6H_6$ and to compare it with the structure of the oxygen-active form. The comparison allows us to postulate a plausible mechanism for the insertion of dioxygen in the [Co(salmhpn)] molecule and to explain the solid-state activity.

Experimental

Preparation of the Dioxygen Adduct.—The dioxygen adduct can be obtained by the method described in ref. 10. The black crystalline material is stable in air for some days but on heating at >50 °C it becomes yellow, regenerating the precursor [Co(salmhpn)]. The same fate occurs to the dioxygen complex when put under vacuum for some hours at room temperature, or on grinding. The compound quickly dissolves in most organic solvents with extensive gas evolution. It was impossible to isolate the adduct from solvents other than benzene.

On the other hand, it is possible to obtain some adduct by oxygenation of a form of the precursor in the solid state. By oxygenation at an O_2 pressure of 800 Torr (*ca.* 1.07 × 10^5 Pa) and room temperature of the monoclinic form obtained from benzene, in a benzene atmosphere, the adduct can be prepared.

Crystals of the dioxygen adduct suitable for *X*-ray analysis can be obtained by dissolving [Co(salmhpn)] in dried and deaerated benzene and exposing this solution to an atmosphere of dry oxygen at 800 Torr and room temperature. Small black prisms form overnight which can be filtered off and washed with benzene. Most crystals show extensive twinning.

Oxygen uptake measurements in the solid state were performed on an apparatus similar to that described in ref. 11.

Crystal Data.—$C_{54}H_{62}Co_2N_6O_6$, M = 1 009.0, Triclinic, space group $P\bar{1}$, a = 17.045(4), b = 12.697(3), c = 11.668(3) Å, α = 94.23(3), β = 90.06(3), γ = 100.43(3)°, U = 2 476 Å^3, D_m = 1.33, Z = 2, D_c = 1.35 g cm^{-3}, graphite-monochromated Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 7.57 cm^{-1}.

Data Collection, Solution and Refinement of the Structure.—A very small but well shaped crystal, with approximate dimensions 0.1 × 0.05 × 0.05 mm was selected and mounted on a Philips automatic diffractometer. A symmetric θ—2θ scan was employed with a scan width of 1.40°, a scan speed of 0.05° s^{-1} and a background time of 20 s, to $\theta_{max.}$ = 20°. Of the intensities collected, 1 482 unique intensities [$I > 2.5\sigma(I)$] ‡ were used in the solution and refinement of the 230 parameters. Three reflections, monitored periodically, did not show any systematic variation in intensity during data collection. The raw intensity data were corrected for Lorentz-polarization effects but not for absorption. Assuming space group $P\bar{1}$, the

† *Supplementary data available* (No. SUP 23704, 14 pp.): structure factors, thermal parameters, H-atom co-ordinates, least-squares planes. See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

‡ The standard deviation on intensity was computed by the formula: $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.02I)^2]^{\frac{1}{2}}$ where P is the total integrated count obtained in time T_p, B_1 and B_2 are the background counts each collected in time T_b, $I = P - 0.5(T_p/T_b)(B_1 + B_2)$, and $0.02I$ is a correction for unrealistically small standard deviations in strong reflections.

Table 1. Final atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for $[\{Co(salmhpn)\}_2]\cdot O_2\cdot 2C_6H_6$

	Dioxygenated molecule (A)			Non-dioxygenated molecule (B)		
Atom	*X/a*	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*
Co	6 315(2)	3 882(3)	7 375(3)	8 799(2)	−467(3)	7 358(3)
O(1)	6 323(11)	3 796(15)	9 004(16)	8 127(11)	−735(15)	5 911(16)
O(2)	6 343(12)	3 926(16)	5 719(16)	8 293(10)	−519(13)	8 876(14)
O(3)	7 438(15)	4 274(19)	7 398(21)			
O(4)	7 892(32)	4 605(42)	8 004(46)			
O(4′)	7 897(29)	3 960(38)	6 954(41)			
N(1)	6 337(14)	2 384(19)	7 229(21)	8 845(14)	1 140(20)	7 325(22)
N(2)	6 320(13)	5 465(18)	7 550(20)	8 823(14)	−2 058(19)	7 262(21)
N(3)	5 071(16)	3 485(25)	7 328(26)	10 088(13)	−223(19)	7 394(21)
C(1)	6 984(11)	2 307(12)	9 031(16)	8 027(11)	1 126(11)	5 632(16)
C(2)	6 782(11)	3 246(12)	9 548(16)	7 883(11)	23(11)	5 335(16)
C(3)	7 040(11)	3 600(12)	10 669(16)	7 433(11)	−392(11)	4 352(16)
C(4)	7 499(11)	3 016(12)	11 273(16)	7 125(11)	297(11)	3 667(16)
C(5)	7 701(11)	2 077(12)	10 755(16)	7 269(11)	1 400(11)	3 964(16)
C(6)	7 444(11)	1 723(12)	9 635(16)	7 720(11)	1 814(11)	4 947(16)
C(7)	6 642(15)	1 823(23)	7 936(23)	8 504(18)	1 610(27)	6 638(26)
C(8)	6 914(11)	5 810(11)	5 762(16)	8 071(12)	−2 417(12)	9 088(17)
C(9)	6 755(11)	4 763(11)	5 251(16)	8 047(12)	−1 359(12)	9 482(17)
C(10)	7 009(11)	4 547(11)	4 137(16)	7 723(12)	−1 140(12)	10 552(17)
C(11)	7 422(11)	5 377(11)	3 532(16)	7 423(12)	−1 979(12)	11 228(17)
C(12)	7 582(11)	6 423(11)	4 043(16)	7 477(12)	−3 037(12)	10 834(17)
C(13)	7 328(11)	6 640(11)	5 158(16)	7 771(12)	−3 256(12)	9 764(17)
C(14)	6 599(16)	6 068(25)	6 837(23)	8 473(17)	−2 693(26)	8 038(26)
C(15)	5 907(19)	1 728(26)	6 217(27)	9 372(20)	1 825(26)	8 268(27)
C(16)	4 957(22)	1 556(31)	6 501(32)	10 277(23)	1 875(31)	8 037(33)
C(17)	4 771(33)	2 371(51)	7 497(52)	10 458(22)	901(33)	7 124(33)
C(17′)	4 670(60)	2 774(87)	6 301(89)			
C(18)	5 814(19)	5 761(24)	8 530(26)	9 248(20)	−2 494(26)	6 298(28)
C(19)	4 962(19)	5 377(27)	8 308(29)	10 092(21)	−2 204(28)	6 542(29)
C(20)	4 710(38)	4 147(59)	8 313(59)	10 393(19)	−961(27)	6 416(27)
C(20′)	4 827(72)	4 790(110)	7 418(124)			
C(21)	4 774(34)	3 997(51)	6 244(52)	10 370(20)	−408(28)	8 592(29)
C(21′)	4 839(60)	3 013(89)	8 635(95)			

	Benzene solvent molecules						
Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
C(1B1)	4 085(16)	1 023(19)	1 068(19)	C(1B2)	9 529(35)	5 152(45)	4 099(46)
C(2B1)	4 911(16)	1 290(19)	964(19)	C(2B2)	9 143(28)	4 657(39)	5 828(48)
C(3B1)	5 395(16)	1 565(19)	1 945(19)	C(3B2)	9 594(37)	4 458(44)	6 091(48)
C(4B1)	5 052(16)	1 573(19)	3 030(19)	C(1B3)	9 171(28)	4 678(41)	9 916(47)
C(5B1)	4 226(16)	1 306(19)	3 134(19)	C(2B3)	9 666(47)	5 326(56)	9 167(53)
C(6B1)	3 742(16)	1 031(19)	2 154(19)	C(3B3)	10 434(38)	5 743(42)	9 320(46)

structure was solved by means of Patterson and electron-density syntheses which gave the positions of all the non-hydrogen atoms.

A series of full-matrix least-squares cycles with isotropic thermal parameters for all the atoms reduced the agreement index to $R = 0.087$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.093$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = k/[\sigma^2(F) + aF^2]$ where k and a are variable parameters refined to 0.8805 and 0.008944 respectively.

As the number of observed reflections is quite low, rigid group refinement was used for the benzene rings of the salicylaldimine moieties and for one solvate benzene. The two benzene molecules interacting with the co-ordinated dioxygen were refined without constraints. The hydrogen atoms bound to the atoms enclosed in the rigid groups were also included in the refinement as well as the hydrogen atoms of the iminic carbon atoms.

The Fourier syntheses showed the presence of six peaks around the N(3A) atom in the oxygenated molecule. This was interpreted in terms of a two-fold orientational disorder around the Co(A)–N(3A) axis in the oxygenated molecule. On the basis of this hypothesis two sets of positions for the atoms C(17A), C(20A), and C(21A) were refined together with their occupancy factors which reached the values of 0.65 and 0.35 respectively. A final Fourier-difference function was featureless.

The program used was SHELX 76 [12] with coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections from International Tables.[13] Final atomic co-ordinates with estimated standard deviations are reported in Table 1.

Inspection of Table 1 shows that standard deviations of the atomic parameters are somewhat large and prevent a detailed discussion of bond lengths and angles. This situation is rather common in crystal structures of dioxygen adducts, where the small number of observed reflections due to the difficulties of obtaining good crystals, the presence of disorder in the dioxygen moiety as well as in other parts of the complex molecules and eventually in the crystallization solvent, do not allow a careful refinement of the structure.[2,5] However, we believe that the essential features of the structure are correct and that the large stereochemical changes accompanying the oxygenation

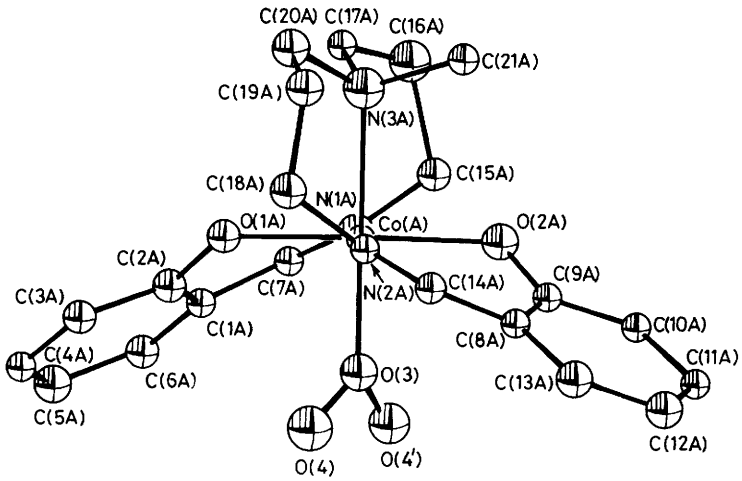

Figure 1. ORTEP drawing of the dioxygenated molecule showing the two-fold orientational disorder of the dioxygen molecule. Ellipsoids enclose 30% probability

process can be confidently discussed. Molecular plots were produced by ORTEP B.[14]

Discussion

Description of the Structure.—The crystal structure of $[\{Co(salmhpn)\}_2]\cdot O_2\cdot 2C_6H_6$ consists of two different types of monomeric complex molecules in a 1 : 1 ratio. Type A molecules (Figure 1) contain dioxygen co-ordinated to the cobalt atom in the end-on bent-bond mode *trans* to the N(3A) atom. Figure 2 shows type B molecules in which the metal centre does not co-ordinate dioxygen.

Four benzene molecules per unit cell fill empty spaces in the crystal lattice. Two of them are in short contact with co-ordinated dioxygen.

Figure 3 shows the packing of all molecules contained in two elementary cells. Bond lengths and angles in the molecules with estimated standard deviations are reported in Table 2.

In type A molecules the metal centre has a pseudo octahedral stereochemistry where the O(1A), O(2A), N(1A), and N(2A) atoms of the Schiff-base ligand are strictly coplanar with maximum deviation of 0.003 Å. The cobalt atom deviates slightly (0.026 Å) towards the apical nitrogen. On the contrary, the atoms N(1A), C(7A) and N(2A), C(14A) deviate significantly from the planes defined by the carbon and oxygen atoms of the respective salicylidene residues. The dihedral angle between the least-squares planes through the salicylidene residues is 115.3°, a value quite close to 118.2 and 120.0° found between the corresponding planes in the two forms of the precursor [Co(salmhpn)] obtained from benzene.[8,9]

The dioxygenated molecules show the presence of a non-crystallographic two fold symmetry axis collinear with the N(3A)–Co(A) bond. As for the structures of the three forms of the precursor [Co(salmhpn)][8,9] and for the structure of the [Ni(salmhpn)] complex,[15] orientational disorder of the molecules about the pseudo-symmetry axis is observed.

The molecules of type B contain five-co-ordinated cobalt atoms with trigonal-bipyramidal stereochemistry. The metal centre is 0.045 Å away from the O(1B),O(2B),N(3B) plane towards N(1B). The co-ordination polyhedron shows some differences with respect to the polyhedra of the precursor [Co(salmhpn)] in each of its three forms. The O(1B)–Co(B)–O(B) angle of 120.4° is appreciably smaller than the value of 129.7° found for the corresponding angle in the solid-state oxygen-active form.[9]

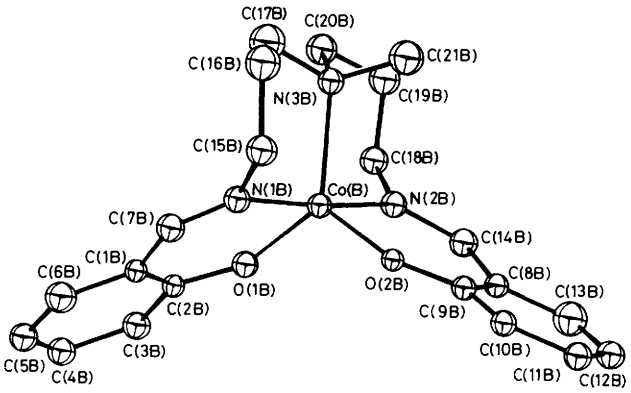

Figure 2. ORTEP drawing of the non-dioxygenated molecule

In type B molecules the atoms of the salicylidene moieties form reasonably good planes with major deviations of 0.031 Å and 0.063 Å for N(1B) and N(2B) respectively. The dihedral angle between the two planes is 119°.

In the case of the non-dioxygenated molecules, the two-fold non-crystallographic symmetry is not present as shown by the values of the angles in the equatorial plane and accurate difference-Fourier analysis did not show any peak around N(3B) in addition to C(17B), C(20B), and C(21B).

The $Co-O_2$ *Geometry and the Role of Benzene.*—The dioxygen molecule is co-ordinated to one cobalt centre and any interactions of pseudo-peroxo-bridge type Co–O–O · · · Co can be excluded, the shortest intermolecular O–O · · · Co distance being 6.14 Å. The closest contacts between bound dioxygen and the non-dioxygenated molecule are O(4) · · · C(13B) 3.32, O(4) · · · C(14B) 3.39, O(4′) · · · C(6B) 3.43, O(4′) · · · C(7B) 3.33 Å (Table 3).

The co-ordinated dioxygen molecule shows an anomalous O–O distance of 1.06(5) Å while the Co–O–O angle [average 135(4)°] is remarkably larger than corresponding values in other Schiff-base cobalt–dioxygen species. However, it is interesting to notice that our values are practically identical to those determined by Robinson and co-workers[5] for [Co(salpeen)(O_2)]·MeCN {salpeen = *NN*′-[2-(2′-pyridyl)ethyl]-

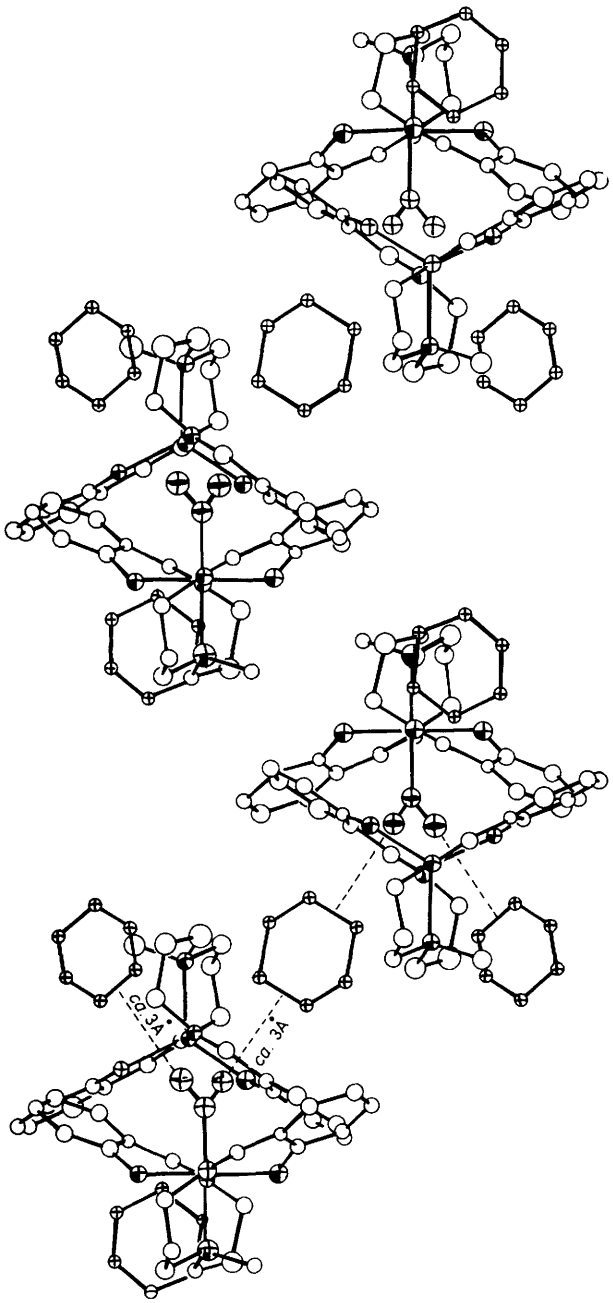

Figure 3. Crystal packing of $[\{Co(salmhpn)\}_2]\cdot O_2\cdot 2C_6H_6$, viewed approximately down the *y* axis

ethylenebis(salicylideneiminate)}. Although the two structures are perfectly in agreement concerning the $Co-O_2$ portion of the molecules, it is probable that disorder of the dioxygen ligand is inferred, so as to explain the anomalous parameters as suggested in ref. 5. A small off-axis displacement of the co-ordinated oxygen atom would lead to a more reasonable O–O bond length and a smaller Co–O–O angle but this model could not be refined by least-squares methods.

The dioxygen group in the present adduct is positioned into channels (Figure 3) formed between the salicylideneiminate groups of the oxygenated and non-dioxygenated molecules. The hydrophobic pocket around a dioxygen molecule is completed by two benzene molecules set on the inversion

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bond lengths

	Oxygenated molecule (A)	Non-dioxygenated molecule (B)
Co–O(1)	1.91(2)	2.01(2)
Co–O(2)	1.94(2)	1.97(2)
Co–O(3)	1.89(2)	
Co–N(1)	1.90(2)	2.03(2)
Co–N(2)	2.00(2)	2.02(2)
Co–N(3)	2.09(3)	2.16(2)
O(3)–O(4)	1.05(5)	
O(3)–O(4′)	1.06(5)	
O(1)–C(2)	1.33(2)	1.34(2)
O(2)–C(9)	1.32(2)	1.33(2)
N(1)–C(7)	1.29(3)	1.24(3)
N(2)–C(14)	1.21(3)	1.33(3)
N(1)–C(15)	1.50(3)	1.53(3)
N(2)–C(18)	1.50(3)	1.47(4)
N(3)–C(17)	1.44(6)	1.51(4)
N(3)–C(20)	1.57(7)	1.57(4)
N(3)–C(21)	1.57(6)	1.53(4)

Solvent benzene molecules *

C(1B2)–C(2B2)	1.40(6)	C(1B3)–C(2B3)	1.42(6)
C(2B2)–C(3B2)	1.52(6)	C(2B3)–C(3B3)	1.33(6)
C(3B2)–C(1B2′)	1.51(6)	C(3B3)–C(1B3′)	1.32(6)

(*b*) Bond angles

	Oxygenated molecule (A)	Non-dioxygenated molecule (B)
O(1)–Co–O(2)	177.4(8)	120.4(7)
O(1)–Co–N(1)	87.6(9)	90.5(9)
O(1)–Co–N(2)	91.7(9)	87.7(9)
O(1)–Co–N(3)	90.7(10)	124.2(8)
O(1)–Co–O(3)	90.2(9)	
O(2)–Co–O(3)	88.2(9)	
O(2)–Co–N(1)	90.5(9)	93.1(9)
O(2)–Co–N(2)	90.2(9)	92.2(9)
O(2)–Co–N(3)	91.0(10)	115.2(8)
N(1)–Co–O(3)	93.4(10)	
N(1)–Co–N(2)	178.5(10)	174.6(10)
N(1)–Co–N(3)	87.9(11)	90.2(10)
N(2)–Co–O(3)	85.2(10)	
N(2)–Co–N(3)	93.4(11)	86.5(10)
N(3)–Co–O(3)	178.4(11)	
Co–O(1)–C(2)	123.7(14)	125.4(14)
Co–O(2)–C(9)	120.2(14)	129.3(13)
Co–O(3)–O(4)	137.4(40)	
Co–O(3)–O(4′)	133.3(40)	
Co–N(1)–C(7)	128.2(22)	127.6(24)
Co–N(2)–C(14)	122.6(23)	121.9(22)
Co–N(1)–C(15)	117.8(19)	114.6(19)
Co–N(2)–C(18)	111.9(18)	117.5(2)
C(7)–N(1)–C(15)	113.9(26)	117.8(28)
C(14)–N(3)–C(18)	124.6(26)	120.6(27)
Co–N(3)–C(17)	113.4(28)	111.9(20)
Co–N(3)–C(20)	110.3(29)	110.3(17)
Co–N(3)–C(21)	107.0(27)	109.0(18)

Solvent benzene molecules *

C(3B2′)–C(1B2)–C(2B2)	130.2(60)
C(1B2)–C(2B2)–C(3B2)	122.2(46)
C(2B2)–C(3B2)–C(1B2′)	107.9(45)
C(3B3′)–C(1B3)–C(2B3)	113.3(45)
C(1B3)–C(2B3)–C(3B3)	127.1(60)
C(2B3)–C(3B3)–C(1B3′)	116.2(45)

* For a benzene molecule (B1) bond distances and angles were fixed at 1.395 Å and 120° respectively.

Table 3. Some significant contact distances shorter than 3.70 Å

(*a*) Within the same asymmetric unit

O(1A) · · · C(17A)	3.34	N(2B) · · · C(20B)	2.99
O(1A) · · · C(19A)	3.46	N(2B) · · · C(21B)	3.36
O(2B) · · · C(6A)	3.48	C(4A) · · · C(1B3)	3.66
O(2B) · · · C(21B)	3.53	C(5B) · · · C(15A)	3.56
O(4) · · · C(3B2)	3.67	C(6A) · · · C(15B)	3.64
O(4) · · · C(1B3)	3.10	C(6B) · · · C(15A)	3.42
O(4) · · · C(2B3)	3.26	C(7A) · · · C(17A)	3.43
O(4′) · · · C(6B)	3.43	C(7A) · · · C(7B)	3.56
O(4′) · · · C(7B)	3.33	C(7A) · · · C(16A)	3.27
O(4′) · · · C(2B2)	3.16	C(7B) · · · C(17B)	3.66
O(4′) · · · C(3B2)	3.04	C(9A) · · · C(21A)	3.56
N(1A) · · · C(6B)	3.68	C(14A) · · · C(19A)	3.29
N(2A) · · · C(20A)	3.11	C(14B) · · · C(19B)	3.26
		C(2B3) · · · C(3B2)	3.67

(*b*) Between atoms in different asymmetric units

(*x*, *y*, *z*) (*x*, *y*, *z* + 1)		($\bar{x}$ + 1, $\bar{y}$, $\bar{z}$ + 1)	
C(21′) · · · C(2B1)	3.61	O(2B) · · · C(6B1)	3.60
(*x*, *y* + 1, *z*)		C(7A) · · · C(6B1)	3.56
O(4) · · · C(13B)	3.32	C(10B) · · · C(1B1)	3.64
O(4) · · · C(14B)	3.39	($\bar{x}$ + 2, $\bar{y}$, $\bar{z}$ + 1)	
C(13A) · · · O(1B)	3.41	C(20B) · · · C(1B)	3.63
C(14A) · · · C(14B)	3.53	C(20B) · · · C(2B)	3.65
C(18A) · · · C(13B)	3.60	($\bar{x}$ + 2, $\bar{y}$, $\bar{z}$ + 2)	
(*x*, *y* − 1, *z*)		C(10B) · · · C(21B)	3.58
N(2B) · · · C(13A)	3.62	($\bar{x}$ + 2, $\bar{y}$ + 1, $\bar{z}$ + 2)	
C(13B) · · · N(2A)	3.65	C(3B3) · · · C(4A)	3.68
C(18B) · · · C(13A)	3.49		

centres of the cell. Each internuclear O–O line is roughly perpendicular to a C–C bond of a benzene molecule which in turn acts as a bridge between two distinct dioxygen molecules. The angles between the lines defined by the couples of atoms O(3)–O(4), C(1B3)–C(2B3) and O(3)–O(4′), C(2B2)–C(3B2) are 83 and 84° while the distances between terminal oxygens and the midpoint of the benzene C–C bonds are 3.10 and 3.00 Å respectively. This particular situation can explain why the compound does not show any well defined loss of solvent and dioxygen on heating, grinding, or under vacuum.[10] The short dioxygen–benzene contact distances may indicate some sort of interaction between O_2 and benzene, as a consequence of dioxygen activation due to the co-ordination. In this connection it is interesting to note that a large amount of experimental work has been devoted to the catalytic oxidations of organic molecules by transition-metal complexes capable of binding dioxygen.[16] Nishinaga *et al.*[17] and Drago and co-workers [18] have shown that [Co(salmhpn)] and its derivatives catalyse dioxygen insertion into 2,6-di-t-butylphenols.

Stereochemical Changes accompanying Oxygenation.—To examine in more detail the stereochemical changes due to dioxygen insertion, it is useful to compare the structure of the adduct with those of the three crystalline forms of the precursor. There are two kinds of changes which affect the stereochemistry of the cobalt atom upon oxygenation: (*a*) a decrease between 0.02 and 0.13 Å of all the metal–ligand bond lengths which can be essentially attributed to a contraction of the cobalt radius on going from a high-spin ($S = \frac{3}{2}$) to a low-spin state ($S = \frac{1}{2}$); [10] (*b*) variations in bond angles due to the transition from a trigonal-bipyramidal to an octahedral stereochemistry. The O_2 addition *trans* to N(3A) forces the O(1) and O(2) atoms to move into a plane containing the N(1A) and N(2A) atoms and roughly perpendicular to the N(3A)–Co(A) bond. Thus the O(1A)–Co(A)–O(2A) angle is 177.4(8)° while the corresponding angles in the α, β, and γ forms are

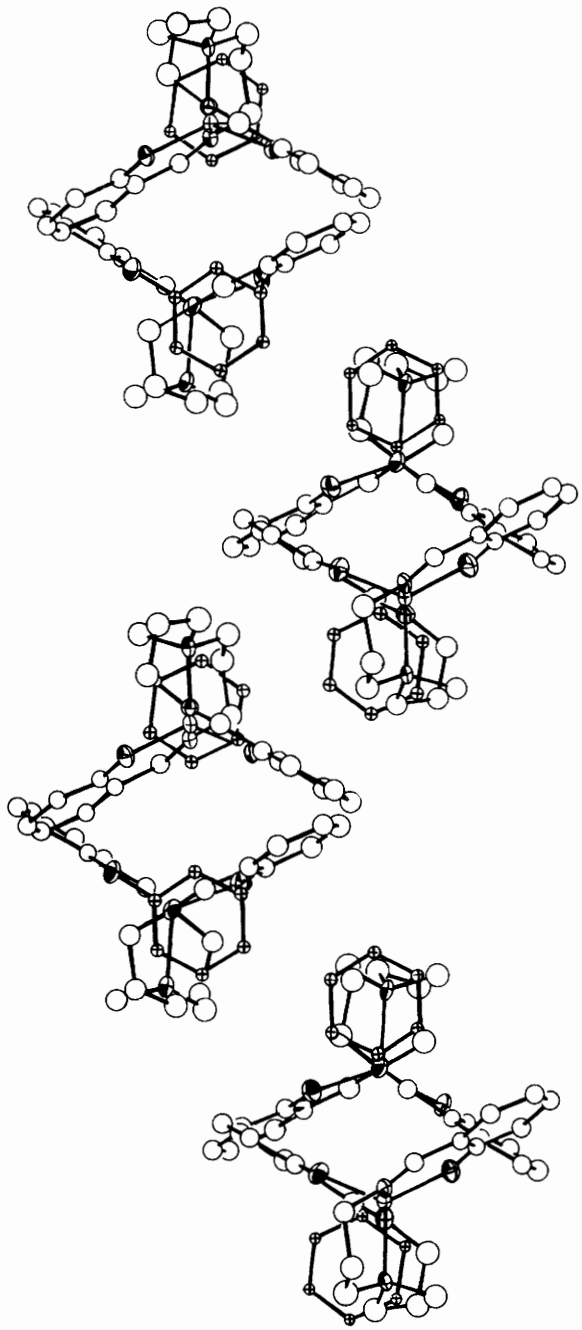

Figure 4. Crystal packing of the precursor [Co(salmhpn)]·C_6H_6, monoclinic (γ)

127.9(3), 126.9(3), and 129.7(4)° respectively. This is the largest angular change so far recorded in a metal atom stereochemistry upon oxygenation. The displacement of the salicylidene oxygen atoms does not influence remarkably the relative position of the two salicyl rings as shown by the values of the dihedral angle between them, which preserves the narrow channels observed also in the γ form of the precursor.

Solid-state Dioxygen Activity.—Figure 4 shows the packing diagram for the γ form. The crystal structures of the γ form and that of the adduct appear strictly similar while major differences exist with the other two structures.[8] This examination induced us to try the reaction with dioxygen in the solid

state, although it was previously affirmed that no absorption occurs. In fact a crystalline powder of the γ form slowly adsorbs dioxygen while the colour changes from brown to black.

Volumetric oxygen uptake measurements were not able to show a definite stoicheiometry of the reaction as the gas uptake is operative at the surface only. The absorption improves slightly on stirring.

The other crystalline forms are inactive towards dioxygen under the same conditions.

Examination of the crystal structure of the γ form reveals that the benzene molecules are coplanar with the O(1)–O(2)–N(3) plane [the angle between the two planes is 8.0(2)°] and a benzene carbon atom points towards the metal centre so that the Co · · · H–C(5B) contact distance was calculated to be 2.94(2) Å.

Moreover, the O(1)–Co–O(2) angle is a little more opened in the γ form than in α and β. Although the differences between the angle in the α and γ or in the β and γ forms [2.8(4)° and 1.8(3)° respectively] are just seven and six times the standard deviations respectively, the above data seem to indicate some sort of activation of the metal centre by the solvent.

Such an interpretation is confirmed by the inactivity towards dioxygen of the α and β forms which either have no benzene at all or the solvent molecule does not show short contacts with the metal centre and is not coplanar with the O(1)–Co–O(2) plane.

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