Crystal and Molecular Structure of (Dioxygen){*NN'*-[2-(2'-pyridyl)ethyl]-ethylenebis(salicylideneiminato)}cobalt–Acetonitrile (1/1)

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The title complex [Co(salpeen)(O_2)]·MeCN crystallises in the monoclinic space group $P2_1/c$ with the unit-cell parameters a = 9.563(2), b = 19.490(4), c = 12.770(3) Å, β = 106.04(2)°, and Z = 4. The structure has been refined using 915 diffractometer-collected reflections having $I > \sigma_I$ to give R 0.128 and R' 0.089. The co-ordination sphere around the cobalt centre is approximately octahedral and the Schiff-base moiety is nearly planar. Dioxygen is co-ordinated in the end-on bent-bond mode and irresolvable disorder and high thermal motion result in an O–O separation of 1.06(3) Å and a $\mathrm{Co{-}O}^{\diagup \mathrm{O}}$ angle of 134(4)°. In contrast to other Co–O_2 structures where the axial base bisects the O–Co–N in-plane right angle, here the pyridyl plane is constrained to bisect the N–Co–N in-plane angle. Marked stereochemical changes accompany the co-ordination of dioxygen to [Co(salpeen)]. Structural evidence is accumulated to support a $\mathrm{Co^{III}{-}O_2^-}$ formulation.

THE geometry of the cobalt–dioxygen moiety in 1 : 1 dioxygen adducts of Schiff-base complexes of cobalt(II) is now well established. From e.s.r. and i.r. spectroscopy an angular geometry, $\mathrm{Co{-}O}^{\diagup \mathrm{O}}$, was inferred.[1] *X*-Ray single-crystal structure analyses [2-8] have confirmed this, and the stereochemistry of these complexes has recently been determined very precisely.[5-7]

There is considerable evidence to support a polarised $\mathrm{Co^{III}{-}O_2^-}$ species rather than a neutral $\mathrm{Co^{II}{-}O_2}$ representation for the dioxygen adducts of d^7 cobalt(II) derivatives of conjugated, quadridentate, dianionic, ligand systems. E.s.r. studies have shown that the unpaired electron resides essentially in a $\pi^*(O_2)$ orbital;[1,9,10] i.r.[11] and *X*-ray crystallographic studies [2,5-7] on the O–O bond indicate a bond order comparable with that of the hyperoxide ion; *X*-ray photoelectron spectroscopy [12] and linear-free-energy relations [13] indicate that electron density is transferred from cobalt to dioxygen. Recently, the conventional interpretation of e.s.r. parameters [1] has been examined,[10] and, for some complexes, a transfer of electron density considerably smaller than previously calculated was deduced. The variation in amount of electron transfer $\mathrm{Co} \longrightarrow \mathrm{O_2}$ indicated that a $\mathrm{Co^{III}{-}O_2^-}$ formulation was not a valid

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[2] (*a*) G. A. Rodley and W. T. Robinson, *Nature*, 1972, **235**, 438; (*b*) A. D. Rae, G. A. Rodley, and W. T. Robinson, unpublished work.

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[13] M. J. Carter, D. P. Rillema, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 392; F. A. Walker, D. Beroiz, and M. Kadish, *ibid.*, 1976, **98**, 3484.

representation in all cases. For the complex [Co(salen)(py)(O_2)], a close relative of [Co(salpeen)(O_2)],* an electron transfer of only 0.5 was proposed.[10]

The conformational changes accompanying the co-ordination of dioxygen are also of interest because of their possible implications in the co-operative binding of dioxygen observed for both haemoglobin and cobalt-substituted haemoglobin.[14]

The preceding paper described the structure of [Co(salpeen)].[15] The dioxygen adduct of this complex, the subject of this paper, has been communicated briefly.[4]

EXPERIMENTAL

Data Collection.—Dark orange-red very thin plate-like crystals were prepared as outlined in ref. 4. Crystal data are: $C_{23}H_{21}CoN_3O_4{\cdot}C_2H_3N$, monoclinic, space group $P2_1/c$;[16] cell dimensions at 24 °C, $a = 9.563(2)$, $b = 19.490(4)$, $c = 12.770(3)$ Å, $\beta = 106.04(2)°$ † for $Z = 4$, $D_c = 1.46$ g cm^{-3} and $D_m = 1.44(1)$ g cm^{-3} (by flotation); absorption coefficient, $\mu = 8.24$ cm^{-1} (Mo-K_α radiation). Infrared spectroscopy and elemental analysis [Found (Calc.): C, 60.2 (59.7); H, 5.1 (4.8); N, 11.7 (11.1%)] supported the formulation as an acetonitrile adduct; ν(O–O) was observed at 1 135 cm^{-1}.

Excluding systematic absences, 1 573 unique reflections for which $2\theta \leqslant 36°$ were collected by the θ—2θ scan technique on a Hilger and Watts automatic diffractometer with zirconium-filtered Mo-K_α radiation. Three standard reflections showed a nett decrease of 10% over the period of data collection; decomposition was not isotropic. The data were scaled accordingly and processed as before.‡ Prior to embarking on limited anisotropic refinement, an absorption correction was applied to the intensity data.

Solution and Refinement of Structure.—From the three-dimensional Patterson synthesis, possible co-ordinates were obtained for the cobalt atom in a general position. Successive cycles of least-squares refinement and difference-Fourier syntheses slowly established the co-ordinates of the remaining non-hydrogen atoms in the [Co(salpeen)(O_2)] species. The two phenyl and pyridyl rings were refined as rigid groups [r(C–N) = r(C–C) 1.39 Å]. A difference-Fourier synthesis based on an isotropic model (R 0.172 for 665 reflections having $I > 2\sigma_I$) revealed an ill defined region of electron density which was interpreted as the adduct molecule, acetonitrile. It was added to the structural model and refinement converged with R 0.114 and R' 0.101.

Analysis of a difference-Fourier synthesis led to relaxation of group constraints and the adoption of anisotropic models for thermal motion of selected atoms. For these final cycles of refinement, phenyl and pyridyl hydrogen-atom positions were calculated [r(C–H) 1.0 Å] prior to each cycle of refinement and included as a fixed contribution to F_c. This model was refined to convergence using 915 reflections having $I > \sigma_I$ so that R 0.128 and R' 0.089. The standard error in an observation of unit weight was 1.45. For the 665 reflections having $I > 2\sigma_I$, R 0.088 and R' 0.076. A decrease in the estimated standard deviations (e.s.d.s) of almost all the parameters accompanied the relaxation of constraints. During the final cycles of refinement the thermal-ellipsoid parameters for C(1) became non-positive definite and those for C(3) highly eccentric. Anomalous interatomic separations in the N(1),C(1),C(2), N(2), C(3),C(4) chain led to an investigation for possible positional disorder. Disordered models were found to be inappropriate and the atoms, when moved to more chemically reasonable positions, returned to their former ' abnormal ' positions.

The ratios of the change in a parameter to its e.s.d. were less than 0.25 : 1 for all the positional parameters and less than 0.4 : 1 for all the thermal parameters except for the adduct molecule, which at all stages refined poorly, where the ratios were less than 1.0 : 1. There was no evidence for secondary extinction among low-angle reflections. The final difference-Fourier map had no prominent features, although there was some residual electron density concentrated around atom C(1), which had physically meaningless thermal-ellipsoid parameters. The standard error in an observation of unit weight (weighting scheme p 0.07) was independent of $|F_o|$ and $(\sin\theta)/\lambda$. Among the ' unobserved ' reflections there were no serious discrepancies between $|F_o|$ and $|F_c|$. Calculated and observed structure factors, thermal parameters, bond distances and angles, intermolecular separations < 3.75 Å, torsion angles, and least-squares planes are available as Supplementary Publication No. SUP 22174 (18 pp.).§ Final positional and thermal parameters for all the atoms are in Table 1. Derived root-mean-square components of thermal displacement along the principal ellipsoidal axes are in Table 2.

General Description of the Structure.—The crystal structure consists of neutral monomeric molecules of the complex, (dioxygen){*NN'*-[2-(2'-pyridyl)ethyl]ethylenebis(salicylideneiminato)}cobalt, and an adduct molecule, acetonitrile. Figure 1 illustrates the complex and defines the atom-labelling system. Figure 2 shows the packing of molecules in the unit cell. Dioxygen is co-ordinated in the end-on bent-bond mode *trans* to the pyridyl ligand. Bond lengths and angles for the approximately octahedral CoL_6 core are contained in Table 3. A more extensive compilation is deposited in SUP 22174.

Atoms O(1), O(2), N(1), N(2) of the Schiff-base ligand system are displaced by at most 0.008(22) Å from their least-squares plane and the cobalt atom is displaced 0.032(4) Å *towards* the co-ordinated pyridyl nitrogen atom, N(3). The two phenyl and one pyridyl groups show no significant deviations from planarity. The approximate coplanarity of the two salicylideneiminate residues is illustrated in Figure 3, which may be compared with Figure

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* Abbreviations: salen = *NN'*-ethylenebis(salicylideneiminate); 3Bu^t-saltmen = *NN'*-tetramethylethylenebis(3-t-butylsalicylideneiminate); 3F-saltmen = *NN'*-tetramethylethylenebis(3-fluorosalicylideneiminate); bzacen = *NN'*-ethylenebis(benzoylacetoneiminate); salpeen = *NN'*-[2-(2'-pyridyl)ethyl]ethylenebis(salicylideneiminate); tpp = *meso*-tetraphenylporphinate; oep = octaethylporphinate; py = pyridine; 1PhCH$_2$-im = 1-benzylimidazole; pip = piperidine; 3Me-py = 3-methylpyridine.

† Here and elsewhere, estimated standard deviations (e.s.d.s) in the least significant figures are quoted in parentheses.

‡ Information on computational procedures and definition of symbols is given in the preceding paper.[15]

§ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[14] (*a*) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384; (*b*) M. F. Perutz and L. F. Ten Eyck, *Cold Spring Harbour Symp. Quant. Biol.*, 1972, **36**, 295; (*c*) R. G. Little and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 4452; (*d*) J. A. Ibers, J. W. Lauher, and R. G. Little, *Acta Cryst.*, 1974, **B30**, 268; (*e*) J. L. Hoard and W. R. Scheidt, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 3919; 1974, **71**, 1578.

[15] G. B. Jameson, F. C. March, Seah Sen Koon, and W. T. Robinson, preceding paper.

[16] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 1.

4 of the preceding paper.[15] With respect to the square-planar N_2O_2 group, these two residues adopt a 'step' conformation similar to that observed for [Co(3Bu^t-saltmen)(1PhCH$_2$-im)(O$_2$)].[5] A selection of dihedral angles between least-squares planes is presented in Table 4.

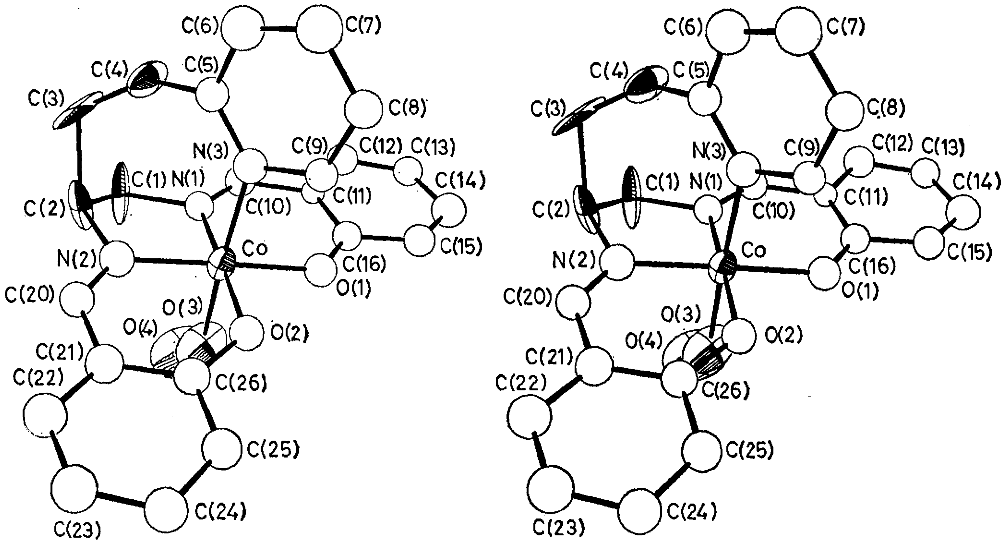

FIGURE 1 Stereoscopic diagram of the complex [Co(salpeen)(O$_2$)] defining the atom labelling. Ellipsoids are drawn at 30% probability. The thermal-ellipsoid parameters for atom C(1) have been adjusted to give a physically meaningful ellipsoid (see text)

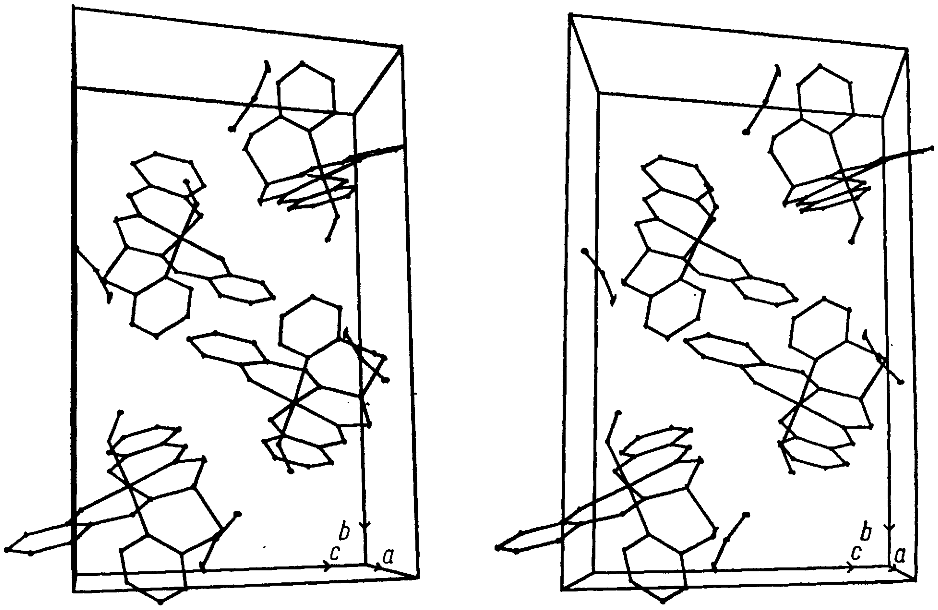

FIGURE 2 Stereoscopic diagram of the contents of the unit cell

The pyridyl group approximately bisects the N(1)–Co–N(2) bond angle. As was observed in the five-co-ordinate precursor, the pyridyl group is rotated about its normal so that, while possible contacts of the ethyl group with the salen plane are relieved, tight C(9)–O(1) and C(9)–O(2) contacts of 2.85(3) Å are created. The constraints imposed by the ethyl bridge lead to the cobalt atom and carbon atom C(4) being, respectively, 0.075(4) and 0.27(4) Å out of the pyridyl plane. In other Schiff-base cobalt dioxygen complexes the plane of the axial base approximately bisects the N(1)–Co–O(1) bond angle.[2,3,5–7]

Non-hydrogen intermolecular separations less than 3.4 Å are: O(2) · · · C(10) 3.27(3), C(10) · · · O(3) 3.22(4), C(20) · · · C(14) 3.40(4), and N(S) · · · C(S2) 3.11(9) Å. The first

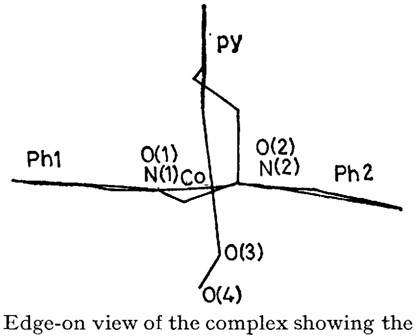

FIGURE 3 Edge-on view of the complex showing the disposition of the salicylideneiminate residues and the pyridyl ring. Atoms N(1) and N(2) eclipse O(1) and O(2), respectively

TABLE 1

Final positional[a] parameters

(a) Non-hydrogen atoms

Atom	X	Y	Z
Co	2 231(4)	1 745(2)	−1 579(3)
O(1)	4 203(18)	2 020(8)	−1 039(13)
O(2)	2 406(18)	1 333(8)	−0 217(13)
N(1)	2 038(23)	2 174(10)	−2 920(17)
N(2)	0 242(24)	1 517(11)	−2 127(19)
N(3)	2 929(24)	0 868(11)	−2 129(19)
O(3)	166(4)	2 527(14)	−100(2)
O(4)	130(5)	3 017(13)	−132(3)
C(10)	304(3)	2 456(13)	−327(2)
C(20)	−055(3)	1 262(14)	−160(2)
C(1)	045(3)	2 197(18)	−368(2)
C(2)	−035(3)	1 713(22)	−332(2)
C(3)	−009(5)	0 978(20)	−412(3)
C(4)	131(4)	0 847(20)	−404(3)
C(11)	457(3)	2 530(12)	−265(2)
C(12)	550(3)	2 825(14)	−321(2)
C(13)	694(3)	2 892(13)	−259(2)
C(14)	748(3)	2 702(14)	−152(2)
C(15)	650(3)	2 386(14)	−106(2)
C(16)	499(3)	2 299(14)	−155(2)
C(21)	−018(3)	1 109(14)	−049(2)
C(22)	−122(3)	0 837(15)	−001(2)
C(23)	−084(3)	0 670(14)	108(3)
C(24)	055(3)	0 705(15)	175(2)
C(25)	158(3)	0 932(13)	127(2)
C(26)	130(3)	1 101(14)	016(2)
C(5)	241(3)	0 521(15)	−308(2)
C(6)	303(3)	−0 108(17)	−321(2)
C(7)	420(3)	−0 389(15)	−249(3)
C(8)	478(3)	−0 018(15)	−152(2)
C(9)	407(3)	0 570(15)	−136(2)
N(S)	−529(5)	1 199(20)	−497(4)
C(S1)	−405(8)	071(3)	−435(4)
C(S2)	−329(5)	016(5)	−396(4)

(b) Hydrogen atoms

Atom	X	Y	Z
H(10)[b]	276	264	−405
H(20)	−162	112	−203
H(12)	514	294	−400
H(13)	760	313	−294
H(14)	853	278	−113
H(15)	691	221	−029
H(22)	−224	075	−047
H(23)	−163	054	140
H(24)	079	054	252
H(25)	259	102	174
H(6)	261	−034	−394
H(7)	457	−084	−261
H(8)	570	−016	−097
H(9)	440	081	−064

[a] Fractional co-ordinates and anisotropic thermal parameters may be generated by placing 0. in front of the first digit. [b] Hydrogen atom H(10) is bonded to carbon atom C(10), *etc.*

two separations are somewhat shorter than van der Waals contact separations (*ca.* 3.4 Å). The high thermal motion of the adduct species indicates that the last separation is a consequence of irresolved disorder in the adduct species.

TABLE 2

Root-mean-square components of thermal displacement (Å) along the principal ellipsoid axes

	R.m.s.		
Atom	1	2	3
Co	0.204(6)	0.239(7)	0.256(8)
O(3)	0.22(5)	0.32(3)	0.49(3)
O(4)	0.18(7)	0.45(4)	0.57(4)
C(1)	*		
C(2)	0.12(9)	0.18(6)	0.47(5)
C(3)	0.05(2)	0.28(7)	0.61(5)
C(4)	0.19(8)	0.24(6)	0.52(5)
N(S)	0.31(6)	0.33(5)	0.61(5)
C(S1)	0.16(10)	0.35(6)	0.53(8)
C(S2)	0.19(9)	0.30(6)	0.99(11)

* Non-positive-definite ellipsoid parameters, but the probable shape is similar to atom C(2).

DISCUSSION

The Adduct $Co-O_2$ *and Ethylene–Ethyl Species.*—The acetonitrile adduct molecule suffers from very high thermal motion and/or disorder. Its stereochemistry is somewhat different to that expected for free acetonitrile. Indeed, we are not entirely certain which is the correct orientation of the molecule; during refinements the middle atom was inclined to drift.

The short O–O separation, the obtuse $\mathrm{Co{-}O}^{\diagup\mathrm{O}}$ angle, and the eclipsed conformation adopted by the $\mathrm{Co{-}O}^{\diagup\mathrm{O}}$ group with respect to the Co–N(1) plane {τ[N(1)–Co–O(3)–O(4)] 3(4)°} are anomalous by comparison with other more precisely determined Schiff-base cobalt–dioxygen species (Table 5).[5-7] Disorder of the dioxygen ligand is therefore inferred. Furthermore, the orientations of the dioxygen thermal ellipsoids suggest disorder similar to that observed for some cobalt–nitrosyl complexes.[17] While artificial resolution of the disorder would lead to a more realistic stereochemistry for the $Co-O_2$ group, the present data do not justify any attempt to quantify the disorder.

TABLE 3

Selected bond distances (Å) and angles (°)

Co–O(1)	1.898(16)	O(1)–Co–N(1)	92.5(9)	O(3)–Co–N(3)	
Co–O(2)	1.882(16)	O(2)–Co–N(2)	93.7(9)	N(3)–Co–O(1)	88.6(8)
Co–N(1)	1.868(21)	O(1)–Co–O(2)	87.6(7)	N(3)–Co–O(2)	90.4(8)
Co–N(2)	1.889(22)	N(1)–Co–N(2)	86.1(10)	N(3)–Co–N(1)	91.1(9)
Co–N(3)	2.029(22)				
Co–O(3)	1.84(3) *	O(1)–Co–N(2)	177.2(9)	N(3)–Co–N(2)	93.9(9)
O(3)–O(4)	1.06(3)	O(2)–Co–N(1)	178.5(9)	N(1)–C(1)–C(2)	108(2)
C(1)–C(2)	1.37(3)	O(3)–Co–O(1)	89.8(12)	N(2)–C(2)–C(1)	115(3)
C(2)–C(3)	1.82(4)	O(3)–Co–O(2)	86.9(11)	N(2)–C(2)–C(3)	107(3)
C(3)–C(4)	1.34(4)	O(3)–Co–N(1)	91.7(11)	C(1)–C(2)–C(3)	100(3)
C(4)–C(5)	1.52(4)	O(3)–Co–N(2)	87.8(12)	C(2)–C(3)–C(4)	113(3)
				C(3)–C(4)–C(5)	127(3)

* When corrected for riding motion, 1.90(3) Å.

The geometry of the ethylene–ethyl bridge is not well defined but the possibility that the peculiarities observed are real cannot be dismissed. When the parameters

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[17] D. Snyder and D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 276.

describing the non-positive definite thermal ellipsoid of C(1) are adjusted by, at most, one e.s.d. the physically meaningful thermal ellipsoid thereby created has a similar aspect to that of C(2), as depicted in Figure 1.* Disorder between two *gauche* conformations has been observed in several related complexes,[2b,18] but in this case the attached ethyl group at C(2) would apparently render this unlikely. No evidence could be found for disorder of C(3) whereby in one variant it is attached to C(1) and in the other to C(2). Such disorder would rationalise not only the ellipsoid eccentricity for C(1), C(2), C(3), and C(4) but also the apparently abnormal bond lengths between these atoms (Table 2). In the absence of such disorder, the ellipsoid eccentricities, but not the unusual separations, may be partially accounted for insofar as C(1) and C(3) possess considerable conformational freedom as was demonstrated by model building. Furthermore, at all the stages of refinement and with two independent data sets, separations significantly different from the expected C–C single-bond length of *ca.* 1.54 Å persisted. It is considered unlikely that these are true bond lengths, but rather that they are artefacts of crystal decomposition, the inadequate description of the adduct species, and the limited and weak data obtained. Nonetheless, in view of the high-pressure conditions used to prepare suitable crystals, the possibility that, in particular, the long C(2)–C(3) bond is real cannot be excluded. Since the two salicylideneiminate residues display no inconsistencies between chemically equivalent bond lengths and angles, it is considered unlikely that refinement has converged to a false minimum.

TABLE 4

Angles between normals to the planes *

I $\bar{d}$ = 0.008	6.1	11.8	89.2	6.0	11.4	3.1	7.7
Ph 1 $\bar{d}$ = 0.015		5.7	95.4	0.1	5.4	3.0	1.6
Ph 2 $\bar{d}$ = 0.025			100.9	5.8	0.6	8.7	4.2
py $\bar{d}$ = 0.024				95.2	100.7	92.3	96.9
sal 1 $\bar{d}$ = 0.014					5.5	2.9	1.7
sal 2 $\bar{d}$ = 0.030						8.4	3.8
Chelate 1 $\bar{d}$ = 0.033							4.6
Chelate 2 $\bar{d}$ = 0.059							

* For a definition of the planes see Table 4 of the preceding paper. $\bar{d}$ (in Å) is the mean absolute displacement of atoms from the plane.

TABLE 5

Stereochemistry of some cobalt dioxygen complexes

	Bond/Å			Angle/°
Complex	r(Co–N$_{ax}$) [a]	r(Co–O$_{ax}$)	r(O–O)	Co–O–O
[Co(bzacen)(py)(O$_2$)] [2 b]	1.99(1)	1.85(2)	1.28(3)	125(2)
[Co(3Bu^t-saltmen)(1PhCH$_2$-im)(O$_2$)] [5]	1.974(8)	1.873(7)	1.27(1)	117.5(6)
[Co(saltmen)(1PhCH$_2$-im)(O$_2$)] [6]	2.011(2)	1.889(2)	1.277(3)	120.0(2)
[Co(3F-saltmen)(1PhCH$_2$-im)(O$_2$)] [7]	2.044(3)	1.881(2)	1.302(3)	117.4(2)
[Co(salpeen)(O$_2$)]	2.03(2)	1.90(3) [a]	*b*	*b*

[a] Corrected for riding motion. [b] Affected by disorder (see text).

Hence the poorly resolved adduct species, the disordered dioxygen ligand, and the peculiarities of the ethylene–ethyl linkage coupled with limited data have all compromised the precision of this structural analysis.

Stereochemical Changes accompanying Oxygenation.—The transformation from distorted trigonal-bipyramidal to octahedral geometry can be considered to be initiated by a movement of atom N(1) into the O(1), O(2), N(2) plane (Figure 3 and Figures 1 and 4 of the preceding paper). The dihedral angles between planes O(1),Co,N(1) and O(2),Co,N(2) change from 25.2 and 30.6° in the five-co-ordinate precursor to 2.9° in the six-co-ordinate dioxygen adduct. This twists the salicylideneiminate residue N(1), C(10), . . . C(16), O(1) into near coplanarity with the other residue. The torsional angle N(1)–O(1)–O(2)–N(2) decreases from 12.6(5) and 17.2(5) to 0.7(7)°; but the changes in torsional angles for the N(1),C(1),C(2),N(2),C(3),C(4),C(5) chain are generally small and not significant. Hence, the pyridyl group is twisted such that the N(1)–Co–N(3)–C(5) torsional angle increases from 29(2) and 27(2) to 46(2)°, and N(1)–Co–N(3)–C(9) decreases from 155(1) and 157(1) to 139(3)°.

Decreases of more than 0.10 Å in Co–N(salen) and between 0.01 and 0.06 Å in Co–O(salen) bond lengths accompany co-ordination of dioxygen. This may be mainly attributed to a contraction of the cobalt radius since [Co(salpeen)] is high spin ($S = \frac{3}{2}$)[15] and [Co(salpeen)(O$_2$)] is low spin ($S = \frac{1}{2}$). The low-spin square-pyramidal complex [Co(salen)(py)] has Co–O(salen) and Co–N(salen) separations of 1.90(1) Å,[18] which are quite similar to those of related six-co-ordinate dioxygen adducts. The large decrease (>0.11 Å) in the Co–N(3) separation is only in part attributable to the spin-state change (see above).

All the dioxygen adducts of cobalt–Schiff-base derivatives share very similar dimensions for the co-ordination octahedron although the Co–N(3) bond lengths are rather more variable (Table 5). These variations cannot be simply attributed to intrinsic differences between an imidazole and pyridyl ligand.

Nature of the Co-ordinated Dioxygen.—Evidence is

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* It is not unusual, when data are limited, for ellipsoid eccentricity to be exaggerated during least-squares refinement.

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

now presented that the Co–O(3) and Co–N(3) separations strongly support a $Co^{III}–O_2^-$ representation.

Although no crystal structures of the type [Co(Schiff base)$(L_{ax})_2]^{n+}$ ($n = 0$ or 1; L_{ax} = imidazole or pyridyl-type base) are known it is not unreasonable to use parameters from analogous porphinato-complexes, despite the Co–L_{eq} separations associated with the Schiff-base equatorial core being *ca.* 0.1 Å shorter. For the complex [Co(oep)$(3Me\text{-}py)_2$] the long Co–L_{ax} separation [2.386(2) Å] [19] is associated with the presence of an electron in the axially aligned $3d_{z^2}$ orbital. A similar separation may be expected for a [Co(Schiff base)-$(py)_2$] species. Removal of the $3d_{z^2}$ electron is accompanied by a marked reduction in r(Co–L_{ax}); for [Co(tpp)$(pip)_2$] r(Co–L_{ax}) is 2.436(2) Å [20] and for [Co(tpp)$(pip)_2]^+$, 2.060(2) Å.[21] Hence for a [Co(Schiff base)$(py)_2]^+$ complex a Co–L_{ax} separation of *ca.* 2.00 Å is reasonable. Moreover, for the complex [Co^{III}(salen)-(py)(OMe)],[22] both the Co–N(py) separation of 2.03(1) Å and the Co–O(OMe) separation of 1.89(1) Å are strikingly similar to the corresponding separations observed in [Co(salpeen)(O_2)] and other [Co(Schiff base)-$(L_{ax})(O_2)$] complexes.

Thus considerable transfer of cobalt $3d_{z^2}$ electron density on to dioxygen *and* a $Co^{III}–O_2^-$ representation is inferred. In further support of this, the non-existence of [Co(Schiff base)(L_{ax})(CO)] species is noted.* Strong axial ligation is associated with the loss of the $3d_{z^2}$ electron either by oxidation or oxidative co-ordination; $[O_2]^-$ is a moderately stable species, $[CO]^-$ is not. Recent semi-quantitative molecular-orbital calculations do not contradict this conclusion.[23]

Conclusion.—The co-ordination of dioxygen to [Co(salpeen)] is characterised by large changes in the stereochemistry about the cobalt centre. The reduction in cobalt–Schiff-base bond lengths may be correlated with a change from a high- to a low-spin species. Axial bond lengths are consistent with an oxidative co-ordination of dioxygen to give a $Co^{III}–O_2^-$ species.

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* Such a species was reported (B. S. Tovrog and R. S. Drago, *J. Amer. Chem. Soc.*, 1974, **96**, 6765) but promptly shown to be an artefact (B. M. Hoffman, T. Szymanski, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **97**, 673).

[19] R. G. Little and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 4440.

[20] W. R. Scheidt, *J. Amer. Chem. Soc.*, 1974, **96**, 84.

[21] W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1973, **95**, 8289.

[22] M. Cesari, C. Neri, C. Perego, E. Perrotti, and A. Zazzetta, *Chem. Comm.*, 1970, 467.

[23] A. Dedieu, M.-M. Rohmer, and A. Viellard, *J. Amer. Chem. Soc.*, 1976, **98**, 5789.