Optically Active Complexes of Schiff Bases. Part 5.[1] An Investigation of some Solvent and Conformational Effects on the Equilibria between Cobalt(II) Schiff-base Complexes and Dioxygen

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The reaction between dioxygen and some cobalt(II) Schiff-base complexes, [CoL], has been studied in dimethylformamide and pyridine [L = ethylene-, 1,2-diphenylethylene-, butane-2,3-diyl-, and 1,2-cyclohexylene-bis-(salicylideneiminato)]. Equilibrium constants for the oxygenation reaction in both solvents have been obtained through manometric and spectrophotometric measurements. Steric effects of conformational origin are indicated and are discussed on the basis of the possible stereochemistry and conformation of the complexes in solution.

In recent years the investigations on the behaviour of simple inorganic models of more complex biological systems have become increasingly important.[2] A variety of biologically active molecules either possess a metal ion as a catalytic centre or need it as a cofactor. Therefore it was hoped that a detailed study of the properties of some model complexes could shed some light on the mechanism of action of metal-containing biological molecules. Reversible addition of dioxygen to metal complexes has been much studied.[3,4] Very recently, models have become increasingly complicated and their behaviour closer to the actual behaviour of the biological oxygen carriers. For instance, it has been shown that iron(II) porphyrin complexes gain reversible

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[1] Part 4, A. Pasini, M. Gullotti, and R. Ugo, *J.C.S. Dalton*, 1977, 346.

[2] See for instance, 'Catalysis Progress in Research,' eds. F. Basolo and R. L. Burwell, jun., Plenum Press, London, 1973.

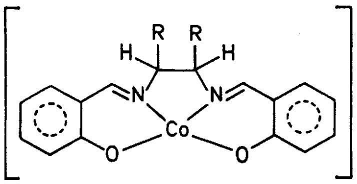
[3] F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

[4] A. V. Savitskij and V. I. Nelyubin, *Russ. Chem. Rev.*, 1975, **44**, 110.

oxygen-carrier properties at room temperature when the iron is sterically protected in such a way that no dimerization between two metal centres can occur.[5,6]

Despite the lack of their occurrence in the respiratory proteins of living systems, cobalt(II) complexes of Schiff bases,[7,8] porphyrins,[9,10] or phthalocyanines [11] have been widely studied as models of oxygen carriers mainly because of the ease of preparation and handling. The ease of investigation, by standard spectroscopic methods, of low-spin cobalt(II) with respect to high-spin iron(II) complexes is well known. As a matter of fact, cobalt(II)-substituted haemoglobin (coglobin) showed a behaviour remarkably similar to that of the original respiratory pigment.[12] In our laboratory we have undertaken a study on the reaction between dioxygen and cobalt(II) complexes of a series of Schiff bases of the ethylenebis(salicylideneiminato) (salen) type,[13] which display conformational aspects,[1] with the aim of gaining a better knowledge of the importance of conformational, and consequently steric, effects on the dioxygen addition.

The complexes used in this work are shown in (1) together with the abbreviations used throughout this paper. Of course, *racemic* or optically active diamines reacted with dioxygen in the same way [the related optically active diamines used for circular dichroism studies [1] all have the same absolute configuration (*S*) in the series (+)bn, (+)chxn,and (−)dpen [1]]. A study of the electronic and conformational properties of these complexes appeared in Part 2 of this series [14] and a detailed discussion of their conformational aspects is to be found in Part 4.[1]



[CoL] (1)

R	L
H	salen
Me	sal(±)- or sal(*m*)- bn
Ph	sal(±)- or sal(*m*)- dpen
$\frac{1}{2}[CH_2]_4$	sal(±)- or sal(*m*)- chxn

RESULTS

We investigated the thermodynamics of dioxygen addition to a solution of complexes (1) in basic solvents. The reactions which occur are believed [8,9,14] to be (1)—(4)

$$\underset{(1)}{[\mathrm{CoL}]} + \mathrm{B} \overset{K_1}{\rightleftharpoons} \underset{(2)}{[\mathrm{CoL(B)}]} \tag{1}$$

$$\underset{(2)}{[\mathrm{CoL(B)}]} + \mathrm{O_2} \overset{K_2}{\rightleftharpoons} \underset{(3)}{[\mathrm{CoL(B)(O_2)}]} \tag{2}$$

$$\underset{(1)}{[\mathrm{CoL}]} + \mathrm{B} + \mathrm{O_2} \overset{K_T}{\rightleftharpoons} \underset{(3)}{[\mathrm{CoL(B)(O_2)}]} \tag{3}$$

$$\underset{(3)}{[\mathrm{CoL(B)(O_2)}]} + \underset{(2)}{[\mathrm{CoL(B)}]} \overset{K_4}{\rightleftharpoons} \underset{(4)}{[\mathrm{(B)LCo(O_2)CoL(B)}]} \tag{4}$$

where B represents a molecule of a base [dimethylformamide (dmf) in case (*a*) and pyridine (py) in case (*b*)]. In solutions of neat pyridine at room temperature the five-co-ordinate adduct (2) is the predominant species (*i.e.* the only species that can be detected by spectroscopic techniques [14,15]), whereas in dmf the equilibrium (1) lies very much to the left and the cobalt(II) complex is present in solution essentially as the four-co-ordinate pseudo-square-planar species (1).[14,15]

However, when oxygen is bubbled through concentrated solutions of (1) in both solvents, the isolated complex is the dimeric μ-peroxo-species (4),[8,14] which is the less soluble species. This species contains two molecules of co-ordinated base even in the dmf case, as shown by elemental analyses, dioxygen evolution,[14] and *X*-ray investigations; [16] consequently it is probably formed *via* a more or less stable five-co-ordinate species (2). Despite this observation the existence of monomeric dioxygen adducts, as the major components of the oxygenated solutions, has been inferred by e.s.r. and manometric measurements,[17,18] and at least in two cases a complex similar to (3) has been obtained in a crystalline form and investigated by *X*-ray diffraction.[19,20,*] It was clear from these studies that, in dilute solutions, the amount of μ-peroxo-bridged species formed through reaction (4) is very low. We have confirmed this finding; consequently we have not considered the formation of dimers in our range of concentrations (10^{-3}—10^{-5} mol dm^{-3}), and we have evaluated by both spectroscopic and gas-volumetric techniques the thermodynamic data of reactions (2) and (3). Details of studies on reaction (1) are

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* *Note added in proof.* New pieces of evidence have recently appeared on the formation of compounds of the type [CoL(B)(O$_2$)] where L is a sterically hindered Schiff base. In this case reaction (4) does not occur and a compound of the type (3) can be isolated in the solid state (R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Christoph, *J. Amer. Chem. Soc.*, 1976, **98**, 5135; A. Avdeef and W. P. Schaefer, *J. Amer. Chem. Soc.*, 1976, **98**, 5153).

[5] J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 1973, **95**, 5757; J. Almog, J. E. Baldwin, and J. Huff, *ibid.*, 1975, **97**, 226.

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[9] F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 1154.

[10] (*a*) H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, 1972, **94**, 1559; (*b*) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *ibid.*, 1973, **95**, 1796.

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[13] M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazzetta*, 1972, **102**, 855.

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

[15] F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, F. Salghetti, and R. Ugo, *Chimica e Industria*, 1971, **53**, 264.

[16] M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.* (*A*), 1970, 1069.

[17] C. Busetto, C. Neri, N. Palladino, and E. Perrotti, *Inorg. Chim. Acta*, 1971, **5**, 129.

[18] M. Green and D. Mettrick, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 149; G. Costa, A. Puxeddu, and L. Nardin Stefani, *ibid.*, p. 191.

[19] G. A. Rodley and W. T. Robinson, *Nature*, 1972, **235**, 438.

[20] M. Calligaris, G. Nardin, L. Randaccio, and G. Tauzher, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 419.

reported elsewhere.[21,22] The results from the variations of the optical absorption and from the measurement of dioxygen uptake were in good agreement, despite the fact that we used different total concentrations of the cobalt complexes (10^{-5} and 10^{-3} mol dm^{-3} respectively). This confirms that, in this range of concentrations, reaction (4) is practically negligible. In the case of dmf solutions we measured only reaction (3), because the equilibrium (1) lies very much to the left. The equilibrium constants which could be directly measured were those of reaction (2) in pyridine and of reaction (3) in dmf. Reaction (1) could be studied in an inert solvent ($CHCl_3$) only for pyridine.[21,22]

In Table 1 are listed values of the equilibrium constants and thermodynamic parameters at 20 °C for reaction (3) (B = dmf). Some of them were determined by the spectrophotometric method and others by the manometric method. When both methods were used the values obtained agreed quite well (*ca.* ±2%). The value of K_T at 20 °C for the *meso*-1,2-diphenylethylenebis(salicylideneiminato) [sal(*m*)dpen] derivative could be obtained only by extrapolating values obtained at higher temperatures where less oxygen was absorbed and the manometric measurements were, therefore, more reliable. In the calculation of K_T the concentration of dmf was taken to be 13 mol dm^{-3} and that of the oxygen[23] 5×10^{-3} mol dm^{-3} at all the temperatures studied, which is quite a good approximation (see Experimental section). In the case of both the *rac*- and *meso*-butane-2,3-diylbis(salicylideneiminato) [sal(±)-bn and sal(*m*)-bn] derivatives an irreversible oxygenation was observed. In the manometric experiments a slow dioxygen uptake started as soon as the complex was dissolved; however, after a period of time dioxygen was taken up at a very high rate, irreproducibly and in an amount higher than given by the stoicheiometry, presumably because of some oxidation of the ligand. A similar phenomenon was observed with the propane-1,2-diylbis(salicylideneiminato) derivative. This phenomenon was less evident when the spectroscopic method was used; the two steps could be separated and consequently the equilibrium constants for the oxygenation of the salbn complexes are evaluated by extrapolation. However, these latter values must be considered only as tentative.

TABLE 1

Thermodynamic data for the reaction [CoL] + dmf + $O_2 \rightleftharpoons$ [CoL(dmf)(O_2)] in dmf at 20 °C. Standard state [O_2] = 1 mol dm^{-3}

L	K_T[a]	$\Delta H_T^{\ominus}$	$\Delta S_T^{\ominus}$	Notes
	dm^6 mol^{-2}	kJ mol^{-1}	J K^{-1} mol^{-1}	
salen	640	−59	−142	*b*
sal(±)dpen	73	−63	−193	*b, c*
sal(*m*)dpen	923	−63	−159	*b—d*
sal(±)chxn	307	−59	−155	*b—d*
sal(*m*)chxn	400	−59	−151	*c*
sal(±)bn	*ca.*150			*b, c, e*
sal(*m*)bn	*ca.*10^3			*b, e*

[a] The mean error was estimated to be less than 5%. [b] Evaluated spectrophotometrically. [c] Evaluated from gas-volumetric measurements. [d] The value of K_T was extrapolated from higher temperatures. [e] See text.

In Table 2 are listed the thermodynamic parameters at 20 °C for reaction (2) (B = py). Here again the dioxygen concentration (4.4×10^{-3} mol dm^{-3})[23] was considered constant in the range of temperatures considered.

In the case of [Co(salen)] we recalculated the literature values[24] of the equilibrium constants for the oxygenation reactions for the standard state [O_2] = 1 mol dm^{-3}. In our experiments we obtained slightly lower values than these and a rather complex behaviour of the [Co(salen)] solution, suggesting the presence of other species. Such complex behaviour was not observed with the other Schiff bases used in this work. Even in pyridine we could not obtain reproducible data in the case of the salbn complexes; a rather fast dioxygen uptake resulted in absorption of a greater amount of dioxygen than predicted by the stoicheiometry.

TABLE 2

Thermodynamic data for the reaction [CoL(py)] + $O_2 \rightleftharpoons$ [CoL(py)(O_2)] in pyridine at 20 °C, evaluated from gas-volumetric measurements. [O_2] = 1 mol dm^{-3}

L	K_2[a]	$\Delta H_2^{\ominus}$	$\Delta S_2^{\ominus}$
	dm^3 mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
salen[b]	$>10^4$	−52	−96
sal(±)dpen	25	−43	−121
sal(*m*)dpen	1 000	−72	−188
sal(±)chxn	231	−54	−138
sal(*m*)chxn	95	−59	−168

[a] The mean error was estimated to be less than 7%. [b] Data from ref. 24 recalculated for the above standard state.

TABLE 3

Thermodynamic data for the reaction [CoL] + py $\rightleftharpoons$ [CoL(py)] in chloroform at 20 °C

L	K_1[a]	$\Delta H_1^{\ominus}$	$\Delta S_1^{\ominus}$
	dm^3 mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
salen	13[b]	−33[b]	−88[b]
sal(±)dpen	3.4	−37	−117
sal(*m*)dpen	3.7	−36	−113
sal(±)chxn	10.4	−27	−71
sal(*m*)chxn	5.6	−31	−88

[a] The mean error was estimated to be less than 2%.[22] [b] Values are approximate because of side reactions.

TABLE 4

Thermodynamic data (calculated from Tables 2 and 3) for the reaction [CoL] + py + $O_2 \rightleftharpoons$ [CoL(py)(O_2)] at 20 °C. Standard state [O_2] = 1 mol dm^{-3}

L	$K_T^{\ominus}$	$\Delta H_T^{\ominus}$	$\Delta S_T^{\ominus}$
	dm^6 mol^{-2}	kJ mol^{-1}	J K^{-1} mol^{-1}
salen	$>10^5$	−85	−184
sal(±)dpen	85	−83	−239
sal(*m*)dpen	3 700	−107	−322
sal(±)chxn	2 300	−81	−209
sal(*m*)chxn	540	−89	−255

We could not measure K_T of reaction (3) in pyridine since, in this solvent, the major species in the solution is either [CoL(py)] or [CoL(py)(O_2)] in the absence or in the presence of dioxygen respectively. We therefore measured the equilibrium constants for reaction (1) (B = py) in an inert solvent (chloroform). The values were obtained spectrophotometrically by the Benesi–Hildebrand method[25]

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[21] L. I. Simandi, Z. Szeverènyi, A. Pasini, P. Bianchi, P. Balzarini, and R. Ugo, *Inorg. Nuclear Chem. Letters*, submitted for publication.

[22] A. Pasini, P. Balzarini, and R. Ugo, unpublished work.

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[24] G. Tauzher, G. Amiconi, E. Antonini, M. Brunori, and G. Costa, *Nature* (*New Biology*), 1973, **241**, 222.

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and will be discussed in detail elsewhere.[21,22] The value of K_T was calculated from K_2 (B = py) taking into account the values of K_1 (B = py) (see Tables 3 and 4 respectively). The values in Table 4 can only be used for a rough comparison since they are derived from values for two reactions measured in two different solvents.

DISCUSSION

The results reported outline both solvent and conformational effects; the latter are related to the configuration of the carbon atoms in the diamine bridge.

The Role of the Solvent.—If we consider the general affinity for oxygen of pyridine or dmf solutions of [CoL] complexes (Table 5), we see that dmf solutions display a higher affinity. This is quite a surprising observation as we know that five-co-ordinate adducts are the reactive species toward oxygen,[8,9,14] and that these species are present in very low concentration in dmf.[14,15] A better comparison could be made if we knew the constants K_T of the overall reaction (3). Unfortunately, in the case of the pyridine adducts, the constants K_T have been evaluated only as a product of K_1 (obtained in chloroform) and K_2 (obtained in neat pyridine). Since it is very probable that both K_1 and K_2 are solvent dependent, the absolute values of K_T must be considered with care.

TABLE 5

Comparison between the oxygen uptake of dimethylformamide and pyridine solutions of [CoL] (about 10^{-3} mol dm^{-3}) at 20 °C and p_{O_2} = 1 atm [a]

	b	
L	dmf	pyridine
salen	0.98	0.98
sal(±)dpen	0.43	0.01
sal(*m*)dpen	0.98	0.85
sal(±)chxn	0.67	0.51
sal(*m*)chxn	0.69	0.30

[a] 1 atm = 101 325 Pa. [b] The degree of oxygenation, *i.e.* the number of moles of dioxygen absorbed by 1 mol of starting complex.

With this limitation in mind, it appears (see Tables 1 and 4) that the equilibrium constants of the overall reaction (3) are all lower in dmf than in pyridine solution, suggesting a very low value of K_1 (B = dmf) in dmf, an equilibrium that in fact we could not measure directly. Consequently the observed order of affinities of the respective solutions must reflect high values of K_2 (B = dmf), which would account for the relatively large affinity for dioxygen of the dmf solutions of the unstable five-co-ordinate cobalt(II) dmf adducts. This is not a surprising observation, because it has been reported that, in a series of five-co-ordinate cobalt(II) porphyrin complexes with donor bases B, the affinity for dioxygen does not follow the basicity of the base B,[9] except for a series of electronically related bases.[3,10] Large effects of dmf as solvent have also been observed on the equilibrium constants of reaction (2) in the case of cobalt(II) porphyrin complexes.[26]

Although use of the van't Hoff equation for the evaluation of the thermodynamic parameters gives values which are not completely reliable, particularly for $\Delta S^{\ominus}$, it is possible to give a general discussion of the above observations. The enthalpy of the overall reaction, $\Delta H_T^{\ominus}$, is always much lower in dmf than in pyridine solution. This probably reflects the situation in step (1) because in these two solvents the differences between the enthalpies of step (2) are probably not large. For instance, in the case of the oxygenation of cobalt(II) protoporphyrin IX dimethyl ester in toluene solution, the following values at 20 °C (standard state $[O_2] = 1$ mol dm^{-3}) have been obtained:[10b] $K_2 = 2.2$ dm^3 mol^{-1}, $\Delta H^{\ominus} = -38.5$ kJ mol^{-1}, and $\Delta S^{\ominus} = -125.7$ J K^{-1} mol^{-1} in the presence of pyridine; and $K_2 = 7.3$ dm^3 mol^{-1}, $\Delta H^{\ominus} = -46.1$ kJ mol^{-1}, and $\Delta S^{\ominus} = -146.6$ J K^{-1} mol^{-1} in the presence of dmf. The observed trends in $\Delta H_T^{\ominus} = \Delta H_1^{\ominus} + \Delta H_2^{\ominus}$ reflects a lower value of $\Delta H_1^{\ominus}$ for B = dmf with respect to B = py, in agreement with the lower strength of the new Co–dmf bond compared to the new Co–py bond in step (1).

The value of $\Delta S_T^{\ominus}$ is more negative in pyridine (Tables 1 and 4), although the magnitude of the solvent effects on this term [chloroform instead of pyridine in step (1)] cannot be evaluated. The relative values of $\Delta S_T^{\ominus}$ may be related to a more negative $\Delta S_1^{\ominus}$ (see Table 3) in pyridine than in dmf, probably related to loss of rotational freedom of pyridine around its C_2 axis once it has been co-ordinated, and to a large reorganization of the ligand geometry and conformation (see later). In agreement with this assumption, $\Delta S_1^{\ominus}$ (B = py) is more negative when the chelating diamine is substituted, corresponding to a larger steric hindrance (see Table 3). Moreover, the formation of a rather polar $Co^{III(\delta+)}$–$O_2^{\delta-}$ linkage could cause solvent reorganization to accommodate charge separations. This reorganization is easier in the very polar dmf medium than in pyridine.[26] Consequently, in dmf a more favourable entropy of oxygen binding is expected, which would correspond to a less negative $\Delta S_2^{\ominus}$ for B = dmf compared with B = py. The combination of both these effects probably results in the more negative values of $\Delta S_T^{\ominus}$ observed in pyridine solution.

In conclusion we propose that step (1) is enthalpically unfavourable in dmf, while step (2) is entropically preferred in the same solvent.

The Effects of Substituents in the Diamine.—From the data in Tables 1—5, some general trends can be seen. The highest affinity for oxygen is displayed by the salen derivative and the oxygenation equilibrium constants (K_2 or K_T) for the complexes containing the *meso* form of the diamine are usually higher than those of the corresponding complexes containing the *racemic* forms, with the exception of the salchxn complexes where the opposite trend is observed in pyridine. Obviously such effects, which are comparable to some reported electronic effects,[27] must be related to the conformations of the

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[26] H. C. Stynes and J. Ibers, *J. Amer. Chem. Soc.*, 1972, **94**, 5125.

[27] M. J. Carter, D. P. Rillema, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 392 and refs. therein.

five-co-ordinate complexes, that is to the absolute configuration of the carbon atoms of the diamine ring.

We have recently investigated in detail the conformations of these and related complexes by circular dichroism (c.d.) spectroscopy.[1] In the square-planar complexes, the Schiff-base ligand is tetrahedrally distorted, and the conformation of the diamine chelate ring is such that the substituents always occupy the axial position with the exception of the sal(±)chxn complex where they must be *trans* equatorial because of the requirements of two fused rings. When the diamine is in its *meso* form one substituent must always be equatorial (see Figure 1). Moreover it has been shown [1] that an inversion of the conformation [Figure 1(*a*)] of the diamine ring occurs in passing to five-co-ordinate complexes of the saldpen derivatives; in this case the substituents of the *racemic* form must be equatorial.[1]

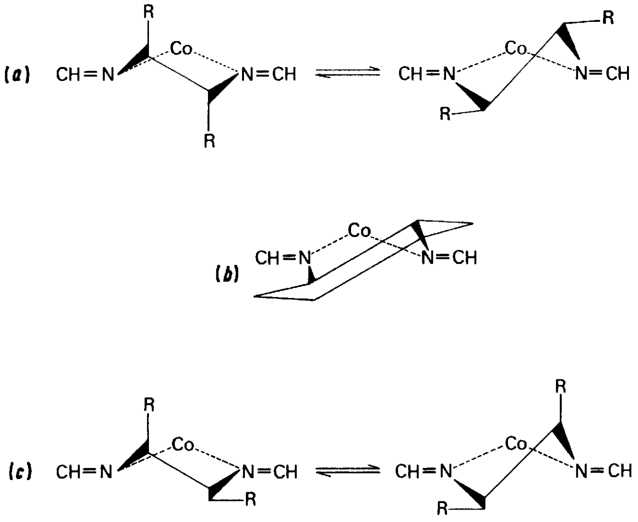

FIGURE 1 Conformation of the diamine chelate ring in square-planar complexes: (*a*) *racemic* and optically active diamines; (*b*) *racemic* and optically active cyclohexanediamine; (*c*) *meso*-diamines

On the basis of these results the observed differences in affinity for oxygen can be related to three factors: (*i*) different stabilities of the five-co-ordinate adducts derived from *rac*- or *meso*-diamine; (*ii*) steric hindrance, arising from axial substituents, towards the dioxygen molecule in the oxygenated complexes; and (*iii*) deformed geometries of the five-co-ordinate species containing the *rac*-diamines, which could produce a lower affinity for dioxygen.

The determination of the equilibrium constants of the five-co-ordinate species (Table 3) has shown that the differences in stability are much smaller than the differences in the affinity for dioxygen as expressed by K_T, at least in the pyridine case. Steric hindrance towards the dioxygen molecule could be important in salbn complexes. In fact, in both five- and six-co-ordinate oxygenated species containing the *rac*-diamine the two methyl groups are axial,[1] whilst with the *meso* form one methyl group must be equatorial, thus producing less steric hindrance at the axial co-ordination sites. However, such an explanation does not take into account the similar behaviour of the related saldpen complexes. With the *racemic* form of saldpen the phenyl groups are equatorial in both five- and six-co-ordinate oxygenated species.[1] In the sal(*m*)dpen complex a larger steric hindrance at the axial co-ordination sites should be produced because one phenyl group must necessarily be axial [Figure 1(*c*)].

Obviously the observed trends in oxygenation must originate from a more complex steric situation. The recent *X*-ray characterization of two very different geometric arrangements of [Co{sal(+)bn}(py)] [28] suggests that the Schiff bases investigated in this work must display a high flexibility. Such flexibility could easily produce both large distortions from planarity of the chelated ligand and different co-ordination geometries.

The five-co-ordinate complex [Co(salen)(py)] has been shown [29] to have a reversed umbrella shape, which does not require a large rearrangement of the quadridentate ligand to attain the final octahedral oxygenated species; but in the presence of substituents on the diamine ring, as in [Co{sal(+)bn}(py)], the chelated ligand exhibits an asymmetric folding, producing a large shielding of the metal atom and requiring a large rearrangement of the ligand and of the metal–ligand bonds in the conversion into the pseudo-planar geometry of the Schiff base in the final octahedral oxygenated species. The origin of the lower affinity for oxygen of complexes derived from *rac*-diamines could be related to the presence of such folding. In complexes which contain the *meso* form the folded structure should produce a diamine chelating ring which is no longer in a real *gauche* conformation. As a consequence the two substituents are in a *cis* arrangement, thus producing a strong reciprocal repulsion. In order to reduce such a repulsion the cobalt complex must prefer the unfolded pseudo-square-pyramidal geometry (with the chelated ring in a *gauche* conformation), which represents a better situation for oxygenation.

This folding effect should not be too evident in the salchxn complexes, where the presence of fused rings induces a greater rigidity of the chelated ligand. Thus it is expected that both $\Delta H_2^{\ominus}$ and $\Delta S_2^{\ominus}$ will favour the oxygenation of complexes containing the *meso*- with respect to *rac*-diamines. Unfortunately, the thermodynamic parameters of oxygenation step (2) could only be evaluated for the pyridine adducts and even in this case with diamines which do not contain methyl substituents (Table 2). Under this limitation we have, as expected, a lower value of $\Delta H_2^{\ominus}$ (B = py) for the *rac*-saldpen complex, although the term $\Delta S_2^{\ominus}$ does not follow the expected trend, with the exception of the salen derivative which has a lower absolute value of $\Delta S_2^{\ominus}$. The entropy term may be affected by an error which is comparable to the contribution due to the effect of the ligand reorganization.

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[28] N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 498.

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

In dmf solution no data on the oxygenation step could be obtained, but it appears that in this solvent the observed trends are more related to entropy, rather than enthalpy, factors, since in the complete oxygenation reaction (3) $\Delta H_T^\ominus$ is nearly constant through the series of complexes considered (Table 1).

Conclusions.—The results discussed above provide evidence for steric effects of conformational origin in the oxygen uptake by cobalt(II) Schiff-base complexes. In iron haemoproteins it has been observed that even small variations of the conformation of the protein part, as in the well known Bohr effect,[30] produce more or less relevant differences in the affinity for dioxygen. Significant variations have also been observed when simple cobalt porphyrin complexes and a series of coglobins are compared.[3,31] In both cases the different affinities must be ascribed mainly to entropy factors.

We have found similar remarkable differences in the stabilities of oxygenated species (corresponding to a factor of *ca.* 20 in our case, compared with 300 in the case of cobalt porphyrins and coglobins [3]) on introducing small, but significant, differences in the molecular complexity. However, in our case the origin of these effects is probably related to the flexibility of the quadridentate Schiff-base ligands, whilst in haemoproteins it must be related to the rigidity of the quadridentate haem ligand or to the significantly favourable contribution that the protein provides to the O_2 bindings,[31] as when coglobins are compared to simple cobalt porphyrin complexes.

The existence of effects of conformational origin in the series of complexes studied has been confirmed by a polarographic investigation of the oxidation of Co^{II} to Co^{III} and the reduction of Co^{II} to Co^{I} in these complexes.[32] Interestingly, some common features were observed (such as the large difference between complexes containing *meso* and *racemic* forms, with the exception of salchxn complexes). It appears that this is a rather general feature of the electron-transfer processes as are, in a certain way, these oxygenation reactions.

EXPERIMENTAL

The cobalt complexes were analysed at the microanalytical laboratory of the University of Milan. Electronic spectra were recorded on a Beckman DK-2A instrument. Pyridine (Carlo Erba RS, permanganate resistant) was stored over K[OH] and distilled before use. Dimethylformamide was boiled *in vacuo* to remove dimethylamine, stored over CaH_2, and distilled under reduced pressure before use. The diamines and the Schiff bases were synthesized as in Part 1 [13] and the cobalt(II) complexes as in Part 2.[14]

Determination of the Equilibrium Constants.—Spectrophotometric. Tubes of known volume fitted with Teflon stoppers were completely filled with known amounts of solutions of the cobalt(II) complexes to which different amounts of oxygen-saturated solvent and degassed solvent were added in order to obtain different [CoL] : $[O_2]$ ratios. The work-up was such as to yield a monophase system; *i.e.* no dead volume was present in the tube. After equilibration for *ca.* 15 h at the appropriate temperature, the solution was carefully transferred to a 1-cm cuvette and the optical absorption was measured at *ca.* 400 nm. The equilibrium constants were evaluated by first calculating from the values of the optical density the degree of oxygenation *Y*, which was then plotted, according to Hill's method,[33] against the initial concentration of oxygen. A typical plot is shown in Figure 2, and Hill's coefficient was always 1 {except in the case of [Co(salen)]}.

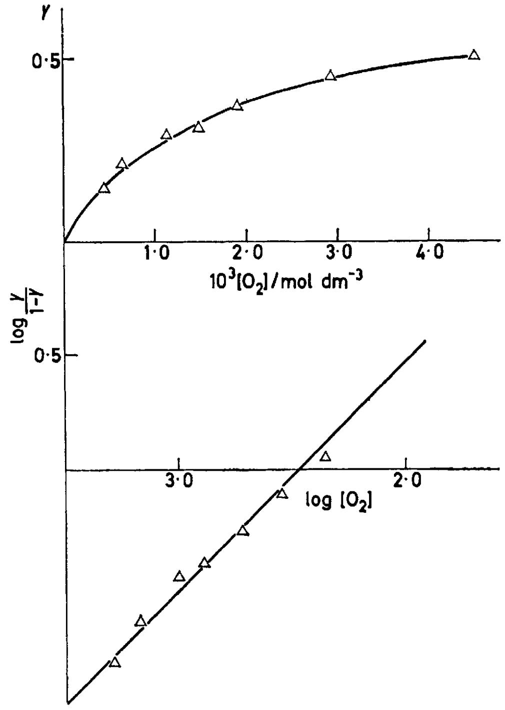

FIGURE 2 Typical Hill's plot for [Co{sal(±)dpen}] in dmf at 20 °C

Manometric. A thermostatted three-necked flask, connected to a gas microburette (5 cm^3, filled with dry oxygen), was fitted with a spoon-shaped glass stopper. A known amount of oxygen-saturated solvent was poured into the flask and a weighed amount of complex was placed on the spoon. After equilibration, the spoon was turned upside down causing the complex to fall into the solvent and, on dissolving, oxygen uptake took place. Vigorous stirring was maintained throughout the experiments to ensure rapid equilibration. The volume of oxygen absorbed by the solution was measured, after further equilibration at atmospheric pressure of the oxygen contained in the burette, by means of a Mariotte connected to the microburette. A cathetometer was used to ensure precision in reading the level of the mercury in the burette–Mariotte system. The equilibrium constants were then evaluated

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[30] See, for instance, E. Antonini and M. Brunori, in ' Frontiers of Biology,' vol. 21, eds. A. Neuberger and E. L. Tatum, North Holland Publishing Co., Amsterdam, 1971, p. 373.

[31] C. A. Spilburg, B. M. Hoffman, and D. H. Petering, *J. Biol. Chem.*, 1972, **247**, 4219.

[32] G. Costa, personal communication; G. Costa and J. Hanzlick, presented at the Meeting on Stability and Reactivity of Coordination Compounds, Bressanone, August 1974, communication 27.

[33] A. V. Hill, *J. Physiol.*, 1910, **40**, 4.

by a simple stoicheiometric balance. A schematic drawing of the apparatus is shown in Figure 3.

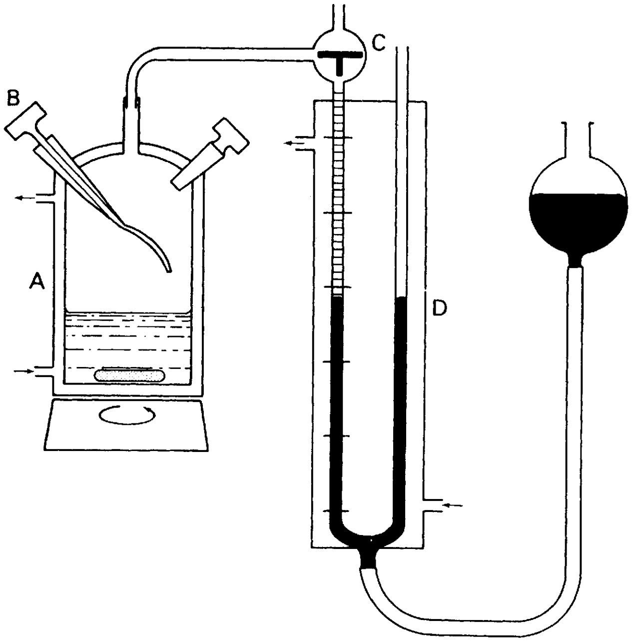

FIGURE 3 Apparatus for the manometric measurements: A, thermostatted flask; B, 'spoon-shaped' stopper; C, three-way tap; D, thermostatted burette–Mariotte system

In both methods of determining the stability constants the concentration of oxygen in dmf and pyridine was considered to be 5.0 × 10^{-3} and 4.4 × 10^{-3} mol dm^{-3} respectively. These values were obtained from Bunsen's coefficient at 18 °C.[23] They are considered to be constant over the temperature range studied (10—40 °C); this approximation is fair since, for instance, in dmf at 26 °C the concentration of oxygen has been reported to be 4.9 × 10^{-3} mol dm^{-3}.[26] The thermodynamic parameters of the reaction with oxygen were obtained by measuring the equilibrium constants at different temperatures. A typical van't Hoff plot is shown in Figure 4.

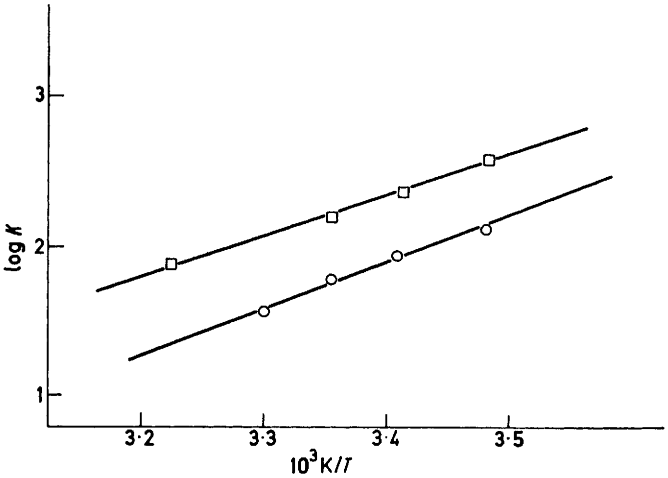

FIGURE 4 Typical van't Hoff plots of K_2 (B = py) in pyridine for [Co{sal(±)chxn}](□) and [Co{sal(*m*)chxn}](○)

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