X-Ray and Electrochemical Investigation on a Series of Cobalt(II) Complexes with Quinquedentate Ligands and their Reactivity towards Dioxygen [†]

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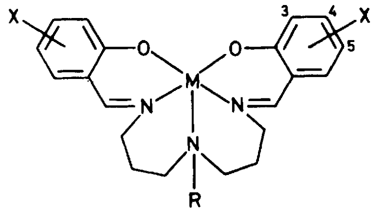
Cobalt(II) complexes with various derivatives of the linear quinquedentate ligand bis(salicylideneimine-3-propyl)amine have been prepared and their electrochemical behaviour and reactivity with dioxygen have been studied in dimethyl sulphoxide solution by cyclic voltammetry. A linear correlation was found between the cobalt(II)–cobalt(III) half-wave potentials ($E_{\frac{1}{2}}$) and the logarithms of the electrochemically determined equilibrium constants for the formation of the 1 : 1 dioxygen adducts. Steric and conformational effects are also discussed in the light of the structure of the oxygen active form of the bis(salicylideneimine-3-propyl)methylamine derivative which has been determined from three-dimensional *X*-ray diffractomer data. Crystals of the compound are monoclinic, space group $P2_1/a$, with a = 13.275(3), b = 16.476(4), c = 11.483(3) Å, β = 94.71(4)°, and Z = 4. The structure has been refined by least-squares techniques to R = 0.108 for 1 366 unique reflections with $I > 3\sigma(I)$. The co-ordination geometry around the cobalt atom can be described in terms of a distorted trigonal bipyramid formed by the three nitrogen and the two oxygen atoms of the ligand molecule.

The quinquedentate ligands derived from substituted salicylaldehydes and bis(3-aminopropyl)amine form with 3*d* transition metals (M) a series of five-co-ordinate complexes [1] [ML] [see below: R = H, X = H (L^1), 3-OMe (L^2), 4-OMe (L^3), 5-OMe (L^4), 5-Cl (L^5), or 5-NO_2 (L^6); R = Me, X = H (L^7), 3-OMe (L^8), 4-OMe (L^9), 5-OMe (L^{10}), 5-Cl (L^{11}), or 5-NO_2 (L^{12})].



X-Ray analyses on two nickel(II) complexes have shown in both cases a distorted trigonal bipyramidal co-ordination around the metal atom with the oxygen and the amino nitrogen atoms in the equatorial plane and the other two nitrogen atoms in the *trans*-axial positions.[2,3]

The cobalt(II) complexes with these ligands have always attracted large interest because of their ability to bind reversibly dioxygen.[4,5] It has also been shown that these complexes can act as catalysts in the selective oxidation of substituted phenols.[6] Several dioxygen adducts have been isolated in the solid state and characterized by means of spectral and magnetic measurements,[7,8] and two of them have been studied by single-crystal *X*-ray analysis.[9,10]

E.s.r. measurements have shown that addition of dioxygen is accompanied by the transfer of a certain amount of electron density from the cobalt centre to the half-filled π* orbitals of the ligand.[11] It should be expected therefore that the electron density on the metal is an important factor in determining O_2 affinity. In agreement with the above considerations, linear correlations have been found between the cobalt(II)→cobalt(III) oxidation potentials and the log of the oxygenation equilibrium constant for several cobalt(II) complexes.[12,13] On the other hand, similar electrochemical investigations have shown that steric effects also play an important role in determining the rate and the equilibrium constant of the oxygenation reaction.[14] We wish to report here an electrochemical investigation on a series of cobalt(II) complexes with the ligands L, with the aim of studying the effects of electron-donating and electron-withdrawing groups on the ease of oxidation of the central metal atoms and to correlate it with the oxygenation equilibrium constants. We report also the crystal and molecular structure of the precursor complex [CoL^7] which appears essential for the interpretation and the discussion of the mechanism of the oxygenation reaction. It should be pointed out that [CoL^7] can be obtained in three crystalline forms. Two of them, an orthorhombic form from benzene and a monoclinic one from acetone, react reversibly with dioxygen in non-aqueous solution and their structures have been reported elsewhere.[15] Only the monoclinic form here described, obtained from benzene, reacts reversibly with dioxygen also in the solid state.

Experimental

Synthesis and Oxygen Uptake Volumetric Measurements.—All the complexes were prepared according to refs. 1—4. Also the 4-OMe complexes, which have not been previously described, were prepared by a similar procedure. Oxygen uptake measurements were carried out with an apparatus similar to that described in ref. 16.

The compounds were dissolved or suspended in degassed dimethyl sulphoxide (dmso) and oxygenated at an O_2 pressure of 760 Torr at 20 °C. The reference flask was filled with the same volume of dmso used for the solutions of the complexes.

X-Ray Analysis.—Recrystallization of [CoL^7] from benzene solutions gave first the less soluble monoclinic form as dark brown prisms. From the filtrate the orthorhombic form separated slowly.[15] A fragment of the monoclinic form with approximate dimensions 0.1 × 0.1 × 0.05 mm was oriented on a Philips PW 1100 automatic diffractometer. Crystal data and intensity collection procedures are reported in Table 1. Three reflections, monitored periodically, did not show any appreciable variation in intensity during data collection. However, some efflorescence occurred during data collection,

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[†] *Supplementary data available* (No. SUP 23641, 11 pp.): thermal parameters, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 Torr = (101 325/760) Pa.

probably due to a superficial loss of benzene. Intensities were corrected for Lorentz polarization effects. The structure was solved by means of Patterson and Fourier syntheses which gave the positions of all the non-hydrogen atoms. Three cycles of least-squares refinement with isotropic temperature factors, followed by two cycles with anisotropic temperature factors for the atoms of the co-ordination polyhedron, reduced the *R* factor to 0.108. 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 factors.

Table 1. Crystal data and intensity collection procedures for the monoclinic form of $[CoL^7]\cdot C_6H_6$

Molecular formula	$C_{21}H_{25}CoN_3O_2\cdot C_6H_6$
M	488.50
Crystal symmetry	monoclinic
Space group	$P2_1/a$
a/Å, *b*/Å, *c*/Å	13.275(3), 16.476(4), 11.483(3)
β/°	94.71(4)
U/Å^3	2 503.1
Z	4
D_c/g cm^{-3}	1.297
μ(Mo-K_α)/cm^{-1}	7.43
λ(Mo-K_α)/Å	0.7107
Monochromatisation	Graphite monochromator
Scan type	θ—2θ symmetric
Scan width/°	1.40
Scan speed/°s^{-1}	0.05
Background time/s	20
$\theta_{max.}$/°	20
Number of unique intensities $[I > 3\sigma(I)]$ [a]	1 366
Number of parameters refined	140
Final *R*, *R'* [b]	0.108, 0.116

[a] The standard deviation of an intensity was calculated as follows: $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.02I)^2]^{\frac{1}{2}}$, where *P* is the total integrated count obtained in time T_p, B_1 and B_2 are the background counts, each obtained in time T_b, $I = P - 0.5(T_p/T_b)(B_1 + B_2)$, and $0.02I$ is an empirical correction for unrealistically small standard deviations in strong reflections. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

In order to reduce the number of parameters, rigid group refinement was used for the solvate benzene and for the benzene rings of the salicylaldimine moieties. The hydrogen atoms bound to these atoms were also included in the group refinement as well as the hydrogen atoms of the two iminic carbon atoms.

The Fourier syntheses showed the presence of six peaks near N(3), about half as high as a carbon atom, which was interpreted in terms of a two-fold orientational disorder of the molecules around the Co–N(3) bond direction. Therefore two distinct sets of positions for C(17), C(20), and C(21) were refined. The occupancy factors for these atoms refined close to 0.4 and 0.6 for the two orientations respectively.

All calculations were carried out with the set of programs SHELX 76 [17] with coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections from the International Tables.[18] Table 2 gives the final atomic co-ordinates with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plot in Figure 1 was produced by ORTEP.[19]

We believe that the presence of disorder, both in the aliphatic chains and in the solvent molecules, partial loss of benzene during data collection and high thermal motion of the atoms account for the somewhat large value of the *R* factor and of the standard deviations.

Electrochemistry.—Reagent grade dmso (Carlo Erba) was dried with 0.3-nm molecular sieves (Union Carbide). The supporting electrolyte, tetraethylammonium perchlorate (Carlo Erba), was dried in a vacuum oven and used without further purification. Bis(η-cyclopentadienyl)iron(II) (Alfa Products) was used as purchased. Extra pure nitrogen was employed to remove oxygen from tested solutions.

Cyclic voltammetry was performed using a PAR model 170 Electrochemistry System as polarizing unit; the recording devices were either a Houston Instruments model 2000 XY recorder or, for potential scan rates higher than 0.5 V s^{-1}, a Hewlett-Packard model 1123A storage oscilloscope. Cyclic voltammetric tests were performed both with a gold sphere working microelectrode freshly covered with a thin mercury layer, and with a platinum sphere working microelectrode;

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations, for $[CoL^7]\cdot C_6H_6$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Co	953(2)	1 183(1)	7 569(2)	N(1)	2 491(12)	1 047(8)	7 652(11)
O(1)	977(9)	1 613(7)	5 973(10)	N(2)	−573(11)	1 299(8)	7 477(10)
O(2)	1 026(8)	1 758(7)	9 065(9)	N(3)	787(15)	−111(9)	7 653(12)
C(1)	2 768(7)	1 758(7)	5 881(9)	C(8)	−713(7)	2 107(7)	9 210(9)
C(2)	1 766(7)	1 840(7)	5 426(9)	C(9)	305(7)	2 095(7)	9 623(9)
C(3)	1 545(7)	2 215(7)	4 347(9)	C(10)	617(7)	2 468(7)	10 682(9)
C(4)	2 326(7)	2 509(7)	3 721(9)	C(11)	−89(7)	2 853(7)	11 328(9)
C(5)	3 328(7)	2 426(7)	4 176(9)	C(12)	−1 107(7)	2 865(7)	10 915(9)
C(6)	3 549(7)	2 051(7)	5 255(9)	C(13)	−1 419(7)	2 492(7)	9 856(9)
C(7)	3 092(17)	1 346(12)	6 951(18)	C(14)	1 108(14)	1 706(11)	8 153(15)
C(15)	2 944(15)	564(13)	8 683(17)	C(18)	−1 111(16)	860(13)	6 504(18)
C(16)	2 606(18)	−329(14)	8 481(20)	C(19)	−1 092(17)	−77(14)	6 747(19)
C(17)	1 799(33)	−534(26)	7 473(40)	C(20)	11(40)	−420(25)	6 669(41)
C(17′)	1 557(47)	−484(33)	8 632(53)	C(20′)	−350(50)	−334(33)	7 853(54)
C(21)	555(30)	−334(21)	8 838(32)				
C(21′)	935(49)	−413(33)	6 438(51)				
C(1B)	928(11)	4 933(10)	8 175(12)	C(4B)	1 087(11)	3 973(10)	6 197(12)
C(2B)	1 008(11)	5 297(10)	7 089(12)	C(5B)	1 007(11)	3 609(10)	7 282(12)
C(3B)	1 087(11)	4 817(10)	6 100(12)	C(6B)	928(11)	4 089(10)	8 271(12)

Table 3. Bond lengths (Å) and angles (°) in the molecule of $[CoL^7]\cdot C_6H_6$ *

Co–O(1)	1.97(1)	N(1)–C(15)	1.51(2)	C(16)–C(17)	1.55(4)	N(3)–C(20′)	1.59(6)
Co–O(2)	1.96(1)	N(3)–C(17)	1.54(4)	C(16)–C(17′)	1.44(5)	N(3)–C(21′)	1.51(5)
Co–N(1)	2.05(2)	N(3)–C(20)	1.55(4)	O(2)–C(9)	1.32(1)	C(8)–C(14)	1.44(2)
Co–N(2)	2.03(1)	N(3)–C(21)	1.47(3)	N(2)–C(14)	1.28(2)	C(18)–C(19)	1.57(3)
Co–N(3)	2.15(1)	C(1)–C(7)	1.44(2)	N(2)–C(18)	1.47(2)	C(19)–C(20)	1.58(5)
O(1)–C(2)	1.32(1)	C(15)–C(16)	1.55(2)	N(3)–C(17′)	1.58(5)	C(19)–C(20′)	1.60(6)
N(1)–C(7)	1.28(2)						

Co–O(1)–C(2)	128.3(8)	N(3)–C(17)–C(16)	111.0(28)	C(14)–N(2)–C(18)	117.4(15)
Co–N(1)–C(7)	126.8(13)	C(15)–C(16)–C(17′)	114.9(26)	Co–N(3)–C(17′)	110.8(21)
Co–N(1)–C(15)	115.2(12)	N(3)–C(17′)–C(16)	114.9(39)	Co–N(3)–C(20′)	109.8(21)
C(7)–N(1)–C(15)	118.0(17)	O(1)–Co–O(2)	129.8(4)	Co–N(3)–C(21′)	105.4(21)
Co–N(3)–C(17)	110.5(18)	O(1)–Co–N(3)	114.1(5)	C(17′)–N(3)–C(20′)	111.9(31)
Co–N(3)–C(20)	111.0(17)	O(2)–Co–N(3)	116.1(5)	C(17′)–N(3)–C(21′)	113.8(30)
Co–N(3)–C(21)	108.7(15)	O(1)–Co–N(1)	89.4(5)	C(20′)–N(3)–C(21′)	104.7(31)
C(17)–N(3)–C(20)	106.7(25)	O(2)–Co–N(1)	92.0(4)	C(9)–C(8)–C(14)	123.7(8)
C(17)–N(3)–C(21)	105.2(23)	O(1)–Co–N(2)	90.6(4)	C(13)–C(8)–C(14)	116.2(8)
C(20)–N(3)–C(21)	114.6(25)	O(2)–Co–N(2)	88.7(4)	O(2)–C(9)–C(8)	124.2(6)
C(2)–C(1)–C(7)	125.1(9)	N(1)–Co–N(2)	179.0(5)	N(2)–C(14)–C(8)	124.6(15)
C(6)–C(1)–C(7)	114.8(9)	N(1)–Co–N(3)	89.7(6)	N(2)–C(18)–C(19)	110.5(16)
O(1)–C(2)–C(1)	124.4(6)	N(2)–Co–N(3)	89.4(6)	C(18)–C(19)–C(20)	110.0(21)
N(1)–C(7)–C(1)	124.2(18)	Co–O(2)–C(9)	130.2(8)	N(3)–C(20)–C(19)	113.9(30)
N(1)–C(15)–C(16)	107.0(15)	Co–N(2)–C(14)	128.1(11)	C(18)–C(19)–C(20′)	113.7(25)
C(15)–C(16)–C(17)	119.5(22)	Co–N(2)–C(18)	114.5(11)	N(3)–C(20′)–C(19)	110.8(36)

* For the benzene rings bonds and angles were fixed at 1.395 Å and 120° respectively; C–H distances were fixed at 1.08 Å.

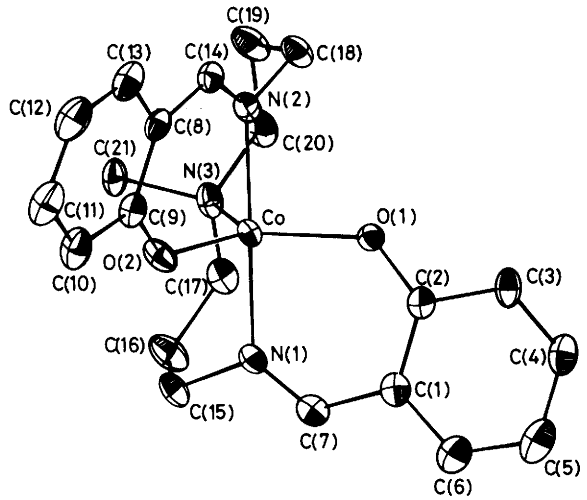

Figure 1. ORTEP drawing of the $[CoL^7]$ molecule showing the atom labelling scheme. Thermal ellipsoids enclose 30% of the electron density

the working electrode was surrounded by a platinum-spiral counter electrode. The potential of the working microelectrode was probed by a Luggin capillary reference electrode compartment.

Controlled potential coulometric tests were performed in a H-shaped cell with anodic and cathodic compartments separated by a sintered glass disc. The working macroelectrode was either a mercury pool or a platinum foil. A mercury pool was used as counter electrode. In these tests an Amel potentiostat model 551, with an associated coulometer Amel integrator model 558, were used.

In all electrochemical tests an aqueous saturated calomel electrode (s.c.e.) was used as reference electrode; the reported potential values refer to it and are believed to be accurate to ±0.01 V. The temperature was controlled at 20 ± 0.1 °C.

The equilibrium data were measured at two different O_2 concentrations by adding two different pressures of oxygen to deaerated solutions in the following way: (1) saturation at P_{O_2} = 760 Torr, by bubbling pure oxygen for 30 min; (2) saturation at supposed P_{O_2} = 152 Torr, by bubbling dry air for 30 min. The reported mean deviations on K_{O_2} values refer to three experiments at P_{O_2} = 760 Torr and/or at P_{O_2} = 152 Torr on each complex.

The solubility of dioxygen in dmso was taken as 1.66×10^{-3} mol dm^{-3} (at 25 °C),[20] assuming the temperature effect on the Bunsen coefficient to be negligible.

Results and Discussion

Description of the Structure.—The crystal structure of monoclinic $[CoL^7]\cdot C_6H_6$ consists of discrete molecules of the complex and of benzene in 1 : 1 ratio. The cobalt atom is co-ordinated by the three nitrogen and the two oxygen atoms of the quinquedentate ligand, arranged in a distorted trigonal bipyramidal environment (Figure 1). The metal atom lies almost exactly in the equatorial plane. Table 3 reports bond lengths and angles in the molecule. The main deviations from the regular trigonal bipyramid are in the equatorial angles O(1)–Co–O(2), O(1)–Co–N(3), and O(2)–Co–N(3) which are 129.8(4), 114.1(5), and 116.1(5)° respectively.

The co-ordination geometry around the cobalt atom is essentially identical with that found in the structures of the two oxygen-inactive forms and corresponding bond lengths and angles in the molecules agree within a few standard deviations.[15] Again, two-fold non-crystallographic symmetry is present about an axis collinear with the Co–N(3) bond direction. Orientational disorder of the molecules about the pseudo-symmetry axis causes two-fold statistical symmetry to be restored at N(3), as shown in Figure 2.

The benzene molecules lie in close proximity of the cobalt atoms on the side of the large O(1)–Co–O(2) angle and are almost coplanar with the equatorial plane of the trigonal bipyramid (Figure 3). The angle between the two planes is 8.1°. The hydrogen atom attached to C(5) of the benzene ring is 2.93 Å distant from the cobalt atom. In the oxygen-inactive form from benzene, the solvent molecules are some distance from the metal atom.[15]

In this connection it may be noted that the O(1)–Co–O(2) angle, which is larger than the other two equatorial angles in all three forms as a consequence of in-plane *d* electron–ligand repulsions,[15] reaches the value of 129.8(4)° in this structure compared with 126.9(3) and 127.9(3)° in the other two forms of [CoL^7].

Electrochemical Oxidation.—All the cobalt(II) complexes studied give rise in dmso solution, both at mercury and platinum electrodes, to an anodic process which in cyclic voltammetry appears as an anodic peak to which a cathodic one is directly associated by reversing the potential sweep. Controlled potential coulometric tests indicate the anodic process to involve a one-electron charge transfer. Cyclic voltammetric data at different scan rates (in the range 0.01—50 V s^{-1}) have been analysed on the basis of the dependence on the scan rate (v) of the anodic peak potential (E_p^a), of the difference between the potential of the anodic peak and that of the directly associated cathodic peak ($E_p^a - E_p^c$), of the ratio of the anodic peak current to the square root of the scan rate ($i_p^a/v^{\frac{1}{2}}$), and of the cathodic to anodic current ratio (i_p^c/i_p^a).[21] In all cases the anodic charge transfer which resulted was quasi-reversible in character.

The cyclic voltammetric responses of [CoL^{11}] reported in Figure 4 illustrate the typical anodic behaviour of the complexes both at mercury and platinum electrodes.

In all cases the process at a platinum electrode occurs with a degree of reversibility considerably lower than that at a mercury electrode. The dependence of the degree of reversibility on the electrode material could be explained by assuming the electrode oxidation of the complexes either to proceed through an inner-sphere mechanism,[22] or to involve the formation of stabilized mercury intermediates at the mercury electrode surface.[23]

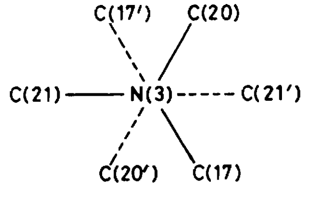

Figure 2. Schematic view along the Co–N(3) bond direction, showing the disorder about N(3)

In Table 4 the formal electrode potential, $E^{0\prime}$, for the Co^{III}/Co^{II} couple is reported together with the heterogeneous rate constant (k_s) at the standard potential of the couple. Considering that transfer coefficient values have a very slight effect on the displacement of the catho-anodic system along the potential axis, the reversible half-wave potential, $E_{\frac{1}{2}}^{r}$, which is practically equal to the formal electrode potential, $E^{0\prime}$, has been computed to a good approximation by $E_{\frac{1}{2}}^{r} = \frac{1}{2}(E_p^a + E_p^c)$. In the likely event that transfer coefficient values fall in the range 0.3—0.7, the k_s values can be roughly evaluated by Nicholson's treatment.[24] The diffusion coefficients of the cobalt(II) complexes have been obtained by comparison of their cyclic voltammetric responses with that of ferrocene at a platinum electrode; the diffusion coefficients of ferrocene in dmso are not available. However, considering that the dependence of the D value of a species on the medium is mainly affected by the viscosity of the medium, a diffusion coefficient value of $D_0 = D_R = D = 0.5 \times 10^{-5}$ cm^2 s^{-1} has been tentatively attributed to ferrocene in dmso on the basis of the viscosity of dmso with respect to the D values of ferrocene in non-aqueous solvents of different viscosities.[25]

It is observed that electron-donating substituents in the aromatic ring favour the oxidation of the cobalt(II) central ion, while electron-withdrawing groups stabilize the initial oxidation state of the metal. In addition, as expected on the basis of the reduced basicity of tertiary amines, the derivatives containing the ligand with R = Me (L^7—L^{12}) are slightly less oxidizable than those with R = H (L^1—L^6).

The Hammett relationship, corrected for the presence of two substituents,[26] holds (Figure 5) if the 3-, 4-, and 5-substituents are considered to be respectively *ortho*, *meta*, and *para* with respect to the phenolic oxygen atom; a non-Hammett behaviour holds by considering the same substituents as *meta*, *para*, and *meta*, respectively, with respect to the CH=N group. The result indicates, as it has to be expected, that the electron density on the cobalt metal centre, of which the redox potential is a measure, is enhanced or

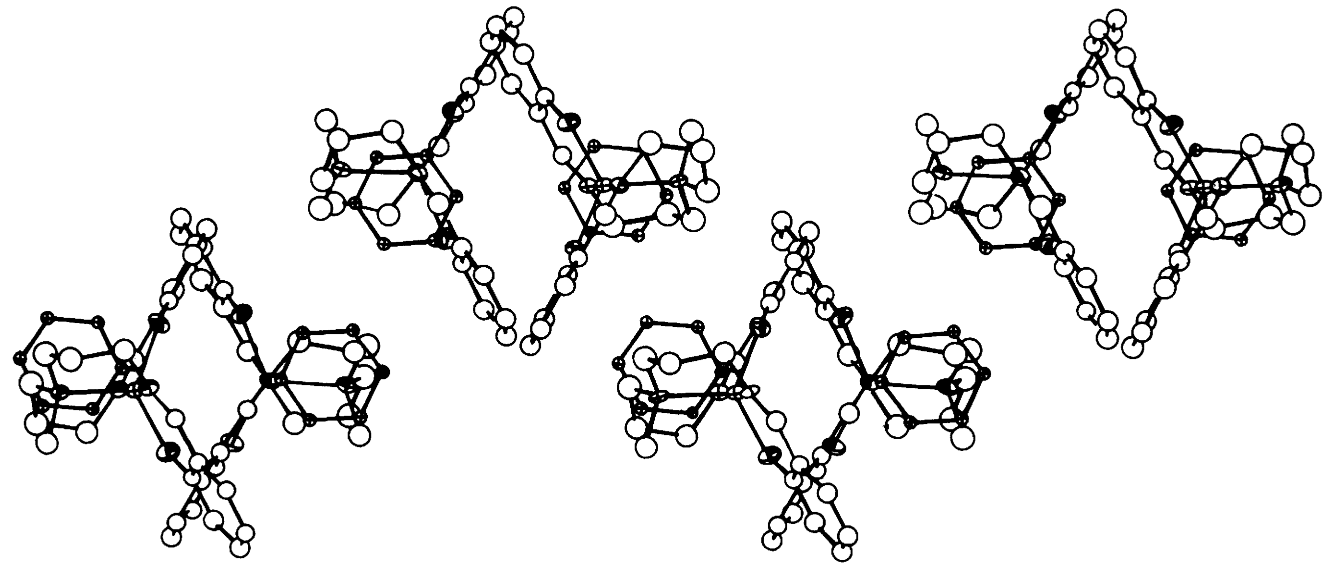

Figure 3. Crystal packing of [CoL^7] and benzene molecules. The view is approximately down the x axis

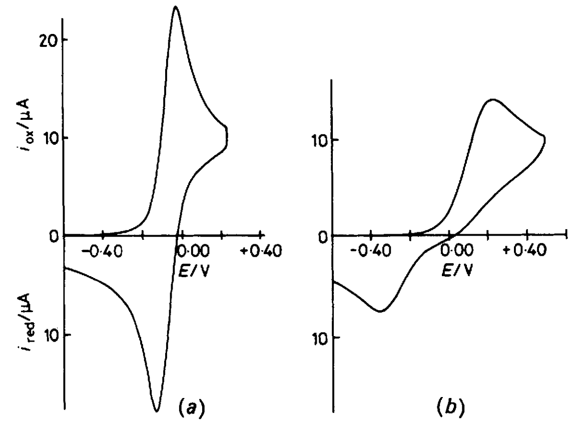

Figure 4. Cyclic voltammograms of a dmso solution containing [CoL^{11}] (1.80×10^{-3} mol dm^{-3}) and [NEt_4][ClO_4] (0.1 mol dm^{-3}) at a mercury electrode (*a*), and at a platinum electrode (*b*). Scan rate = 0.2 V s^{-1} (anodic scan)

Table 4. Electrochemical characteristics of the heterogeneous charge transfer $Co^{II} \xrightarrow{-e^-} Co^{III}$ at a mercury electrode

Complex	R	X	$E^{0\prime}$/V	k_s/cm s^{-1}
[CoL^1]	H	H	−0.27	$(7.0 \pm 0.6) \times 10^{-3}$
[CoL^2]	H	3-OMe	−0.32	$(2.1 \pm 0.5) \times 10^{-2}$
[CoL^3]	H	4-OMe	−0.26	*
[CoL^4]	H	5-OMe	−0.29	$(4.3 \pm 0.6) \times 10^{-3}$
[CoL^5]	H	5-Cl	−0.21	$(1.1 \pm 0.5) \times 10^{-2}$
[CoL^6]	H	5-NO_2	−0.11	$(1.0 \pm 0.5) \times 10^{-2}$
[CoL^7]	Me	H	−0.14	$(1.8 \pm 0.5) \times 10^{-2}$
[CoL^8]	Me	3-OMe	−0.17	$(3.6 \pm 0.5) \times 10^{-2}$
[CoL^9]	Me	4-OMe	−0.14	$(2.2 \pm 0.6) \times 10^{-2}$
[CoL^{10}]	Me	5-OMe	−0.15	$(4.5 \pm 0.7) \times 10^{-3}$
[CoL^{11}]	Me	5-Cl	−0.07	$(1.0 \pm 0.5) \times 10^{-2}$
[CoL^{12}]	Me	5-NO_2	+0.02	$(2.2 \pm 0.6) \times 10^{-3}$

* Quantitative information is prevented due to the partial oxidation in the solid state of this compound.

diminished by phenyl substituents *via* the XC_6H_4–O–Co–O–C_6H_4X pathway.

Oxygen Reactivity.—The generally accepted mechanism for the reaction of dioxygen with cobalt(II) complexes is represented by equations (1) and (2). Although with the complexes of the ligands under study, products isolated from these reactions have the general formula [$(CoL)_2(O_2)$]·solvent, it is commonly accepted that in non-aqueous solutions rapid formation of the 1 : 1 complex takes place,[5,28] followed by a slow reaction which yields the less soluble 2 : 1 species. In this connection it may be noted that the structure of monomeric [$CoL^7(O_2)$][10] shows that insertion of the dioxygen molecule in the end bent-on mode takes place *trans* to N(3) and is indirectly affected by the presence of bulky substituents at the nitrogen atom. The increase of the O–Co–O angle up to 177(1)° causes short intramolecular contacts between the oxygen atoms and the carbon atoms bound to N(3).[29] Attachment of the μ-peroxo bridge, on the contrary,[9] takes place *cis* to N(3) and therefore will be seriously hindered by the presence of a bulky substituent at the nitrogen atom. This mode of dimerization is also confirmed by the structure of the peroxo-*p*-quinolato complex of [CoL^1].[6] Most likely, for a molecule like [CoL] (L = L^1—L^{12}), where the salicylaldimines cannot reach coplanarity due to steric hindrance with the aliphatic chains, μ-peroxo dimerization cannot take place *trans* to N(3). This being the case, conversion from the monomeric dioxygen adduct to the μ-peroxo dimer will involve a rearrangement of the molecular geometry and therefore dimerization will be a slow, temperature-dependent process.

$$[CoL] + O_2 \overset{K_1}{\rightleftharpoons} [CoL(O_2)] \quad (1)$$

$$[CoL(O_2)] + [CoL] \overset{K_2}{\rightleftharpoons} [CoL(O_2)CoL] \quad (2)$$

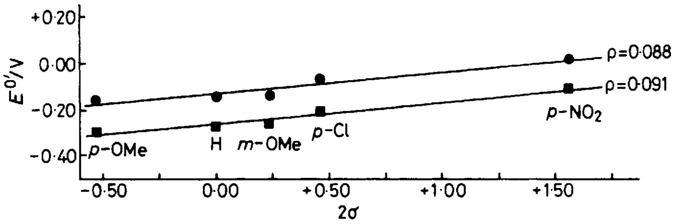

Figure 5. Dependence of the oxidation potential of the cobalt(II) complexes on the substituent constants, σ (values from ref. 27; linear regression analysis); (●) L^7–L^{12} derivatives, (■) L^1–L^6 derivatives

Our oxygen uptake volumetric measurements confirm that for the complexes under study rapid formation of 1 : 1 adducts occurs in dmso solution. Only in the case of the L^2 (R = H, X = 3-OMe) complex a 2 : 1 cobalt : oxygen ratio has been observed together with the formation of a dark brown precipitate. It is likely that the low solubility of the 2 : 1 adduct favours a rapid dimerization.

Equilibrium data for 1 : 1 adducts have been obtained already by polarographic techniques.[14,30] The electrochemical method used here to obtain a rough estimation of K_{O_2} values [K_1 in equation (1)] is based upon the fact that the cyclic voltammetric response of the complexes at a mercury electrode in dmso changes dramatically upon oxygenation. In fact the anodic–cathodic peak system of the compound tends to disappear while a new anodic peak, from a charge transfer coupled to a following chemical reaction (see below), replaces it at higher potential values. In the case of derivatives of L with R = H this peak shifts towards more and more positive potentials to be masked by mercury oxidation. The reaching of equilibrium is shown by the constancy of the peak height relative to the amount of unreacted starting complex. This peak height allows us to calculate the concentration of the non-oxygenated compound and therefore the equilibrium constant. In fact, in the tested scan rate range, both the ratio $(i_p^a)_u/v^{\frac{1}{2}}$ relevant to the amount of unreacted starting complex and the ratio $(i_p^a)_r/(i_p^a)_u$ between the anodic peak currents of reacted and unreacted amounts of complex have constant values; this supports the oxygenation equilibrium being infinitely slow with respect to the cyclic voltammetric timescale. By bubbling nitrogen the initial voltammetric picture is restored completely in the case of derivatives of L with R = Me and partially in the case of derivatives with R = H. This behaviour is illustrated in Figure 6 for [CoL^7], as a typical example.

In order to obtain equilibrium data for each complex at least at two different P_{O_2} values, both ultrapure oxygen (P_{O_2} = 760 Torr) and air (P_{O_2} *ca.* 152 Torr) were bubbled through previously deaerated cobalt(II) complex solutions. The calculated K_{O_2} values are reported in Table 5.

Figure 7 shows that a linear correlation exists between the

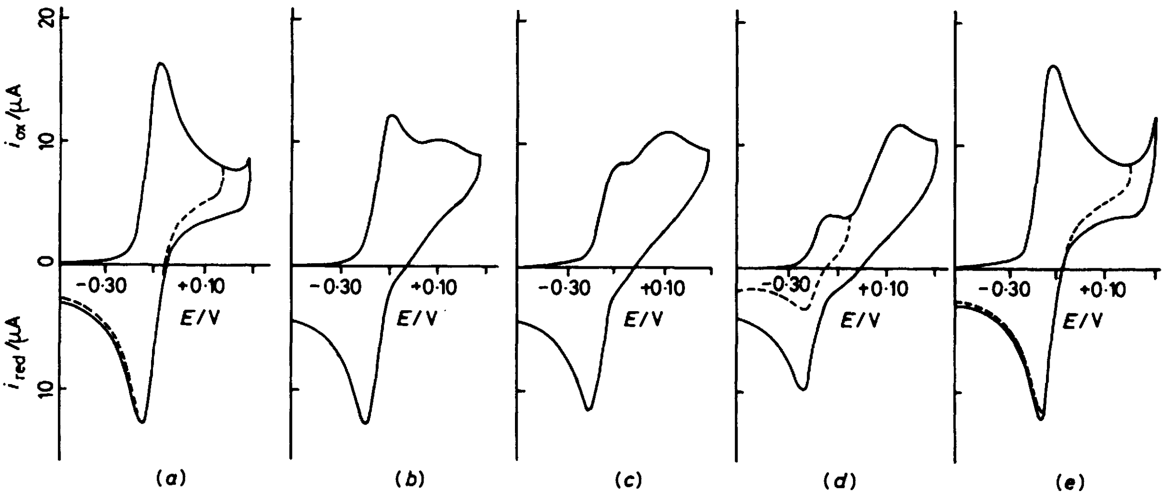

Figure 6. Cyclic voltammetric behaviour of a dmso solution of [CoL^7] (1.14 × 10^{-3} mol dm^{-3}) and [NEt$_4$][ClO$_4$] (0.1 mol dm^{-3}) upon oxygenation. Initial response (*a*); after bubbling O_2 (760 Torr) for 4 (*b*), 6 (*c*), and ≥30 min (*d*); after bubbling N_2 for 10 min (*e*)

Table 5. Equilibrium data for the formation of 1 : 1 adducts between cobalt(II) chelates [CoL] and dioxygen at 20 °C

Complex	K_{O_2}/dm^3 mol^{-1}
[CoL^1]	(7.2 ± 0.6) × 10^4
[CoL^2]	(2.2 ± 0.7) × 10^5
[CoL^3]	*ca.* 8 × 10^4 *
[CoL^4]	> 3 × 10^5
[CoL^5]	(7.5 ± 0.5) × 10^4
[CoL^6]	(2.5 ± 0.6) × 10^4
[CoL^7]	(3.1 ± 0.4) × 10^3
[CoL^8]	(5.8 ± 0.5) × 10^3
[CoL^9]	(5.0 ± 0.6) × 10^3
[CoL^{10}]	(5.6 ± 0.5) × 10^3
[CoL^{11}]	(1.6 ± 0.4) × 10^3
[CoL^{12}]	(1.2 ± 0.3) × 10^2

* See footnote to Table 4.

redox potentials of the complexes and their dioxygen affinity, indicating that also this class of cobalt(II) compounds has an oxygen carrying ability which depends on its ease of oxidation.[5]

As it can be seen, in agreement with their oxidation potentials, derivatives with R = H show a stability with dioxygen one order of magnitude greater than those with R = Me. However, from a quantitative viewpoint this conclusion must be regarded with caution considering that bubbling of nitrogen after oxygenation does not restore completely the starting compounds [CoL] (R = H); the losses in the initial compound are not perfectly reproducible, but typical losses are as follows. For P_{O_2} = 152 Torr, [CoL^5] *ca.* 10%, [CoL^6] *ca.* 15%, [CoL^2] *ca.* 20%, [CoL^1] *ca.* 40%, [CoL^4] ≥ 70%; for P_{O_2} = 760 Torr, [CoL^5] *ca.* 40%, [CoL^6] *ca.* 20%, [CoL^1] *ca.* 50%, [CoL^4] *ca.* 90%.

On this basis we consider that only the derivatives [CoL] (R = Me) can act as oxygen carrier. The ability to take up oxygen for [CoL] (R = Me) derivatives (log K_{O_2}) as a function of the inductive effects of the aromatic ring substituents is reported in Figure 8.

As expected, the Hammett thermodynamic relationship is obeyed, indicating that electronic effects of the substituents also affect the oxygenation reaction, electron-donating groups favouring the 1 : 1 adduct formation. Conversion of the electrochemical reaction constant for the anodic oxidation of R = Me derivatives, $\rho_{emf.}$ = 0.088 V, to the thermodynamic scale[26] gives ρ_{ox} = 1.52. By comparing this value with the thermodynamic reaction constant for the addition of dioxygen to the complexes [CoL] (L = L^7—L^{12}), ρ_{O_2} = −0.828, it can be deduced that the electrochemical oxidation of these cobalt(II) chelates is more sensitive to the electronic effects of phenyl substituents than the addition of dioxygen.

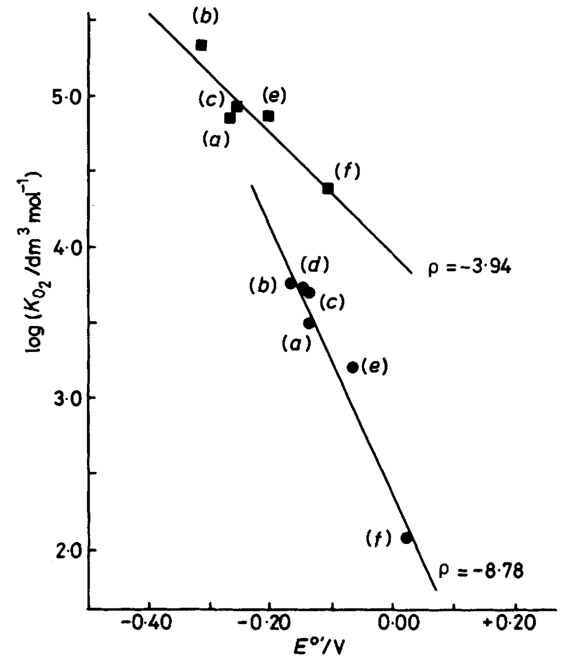

Figure 7. Comparison of oxygen uptake (log K_{O_2}) at 20 °C for Co^{II} with the half-wave potentials: (●) L^7–L^{12} derivatives, (■) L^1–L^6 derivatives; X = H (*a*), 3-OMe (*b*), 4-OMe (*c*), 5-OMe (*d*), 5-Cl (*e*), and 5-NO_2 (*f*)

Although monomeric cobalt(II) dioxygen adducts are often formulated as cobalt(III)-superoxo (Co^{III}–O_2^-) complexes, recently the interpretation of the e.s.r. cobalt hyperfine coupling constants on the basis of a 'spin-pairing' model has shown that the actual charge transferred to O_2 is much smaller than previously calculated. For the complexes

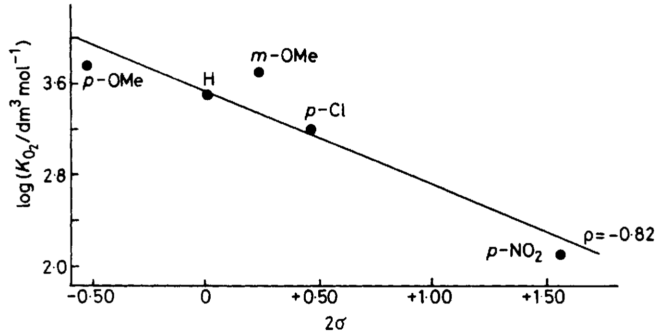

Figure 8. Plot of log K_{O_2} *versus* 2σ for the addition of dioxygen to [CoL] (L = L^7-L^{12})

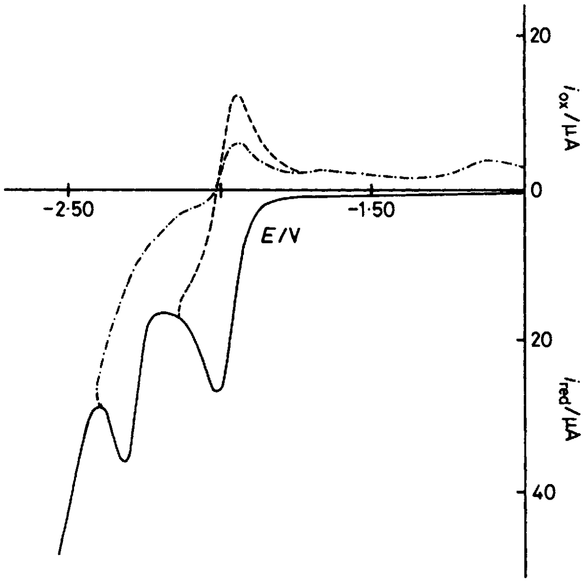

Figure 9. Cyclic voltammetric curve recorded on a dmso solution containing [CoL^7] (1.43 × 10^{-3} mol dm^{-3}) and [NEt_4][ClO_4] (0.1 mol dm^{-3}) with a mercury electrode. Scan rate = 0.2 V s^{-1} (cathodic scan)

Table 6. Potential values for the cathodic reduction of cobalt(II) complexes

Complex	$E^{0\prime}$/V ($Co^{II} \xrightarrow{+e^-} Co^I$)	$E_p{}^b$/V ($Co^I \xrightarrow{+e^-} Co^0$)
[CoL^1]	−2.08 [a]	−2.40
[CoL^2]	−2.06 [a]	−2.36
[CoL^3]	−2.14 [a]	−2.41
[CoL^4]	−2.07 [a]	−2.29
[CoL^5]	−2.05 [b]	−2.13
[CoL^7]	−1.95 [a]	−2.32
[CoL^8]	−2.02 [a]	−2.36
[CoL^9]	−2.06 [a]	−2.44
[CoL^{10}]	−2.06 [a]	−2.29
[CoL^{11}]	−1.88 [a]	−2.17

[a] Value at scan rates in which the $i_p{}^a/i_p{}^c$ ratio reaches unity, indicating that the complications from coupled chemical reactions are overcome. [b] Peak potential value at v = 0.2 V s^{-1}.

[CoL] (L = L^1—L^6) a transfer of about 0.5 electron was deduced.[11]

The involvement of superoxide ions in complex formation reactions can be investigated to some extent by electrochemical techniques. In fact, free superoxide ions can be easily electrogenerated in non-aqueous solvents *via* the cathodic reduction of oxygen, and their complexation by species present in solution can be followed by electrochemical methods. The electrochemical method is based on the fact that when superoxide ions are involved in a complexation step a cathodic process appears at potentials less negative than those relevant to the one generating free superoxide ions, *i.e.*, $O_2 \overset{+e^-}{\rightleftarrows} O_2^-$, and/or this last process appears as irreversible in character.[31-33]

The results of the present study seem to indicate that neither Co^{III} nor superoxide ions are involved to a considerable extent in the complex formation reaction. In fact, upon oxygenation, (*a*) the anodic peak due to [$Co^{II}L$] $\xrightarrow{-e^-}$ [$Co^{III}L$] charge transfer is replaced by another anodic peak (see Figure 6), very likely attributable to [$Co^{II}L(O_2)$] $\xrightarrow{-e^-}$ [$Co^{III}L(O_2)$] oxidation, (*b*) a cathodic peak sufficiently distinct from that relevant to the $O_2 \rightleftarrows O_2^-$ is not present, and (*c*) the $O_2 \rightleftarrows O_2^-$ step still appears as a catho-anodic system.

In addition Figure 6 suggests that [$Co^{III}L$] complexes have no affinity for dioxygen, since the cathodic peak associated to the anodic peak for [$Co^{II}L(O_2)$] oxidation is placed at the same potentials as that of the reduction of [$Co^{III}L$], indicating that in the time span of the cycle dioxygen is completely released from [$Co^{III}L(O_2)$] species.

Electrochemical Reduction.—Although the main electrochemical interest of the present study has been focused on the anodic behaviour of the complexes because of the discussed correlation between ease of oxidation of the central cobalt(II) ion and dioxygen reactivity, a brief investigation on their cathodic behaviour has been carried out also. All complexes display cathodic responses at mercury electrodes which indicate the occurrence of two successive reduction processes. In Figure 9 the cyclic voltammogram of [CoL^7] in the cathodic region at a mercury electrode is given as an example.

The analysis of the cyclic voltammetric data at different scan rates implies that the less cathodic process involves a quasi-reversible one-electron charge transfer complicated by coupled following chemical reactions, while the more cathodic one consists of a one-electron step irreversible in character. It is reasonable to attribute the two processes to the $Co^{II} \xrightarrow{+e^-} Co^I$ and $Co^I \xrightarrow{+e^-} Co^0$ steps, respectively. Only in the case of nitro-substituted compounds does the electroreduction of the NO_2 group interfere with the mentioned cathodic picture. The reduction potentials of the cobalt(II) derivatives studied are reported in Table 6.

Also the charge transfer $Co^{II} \xrightarrow{+e^-} Co^I$ appears to be sensitive to electronic effects of the phenyl substituents. In the case of the derivatives L^7—L^{12}, where there is a more complete set of data, a comparison of ρ for the reaction $Co^{II} \rightleftarrows Co^I$ (0.131 V), with that for the reaction $Co^{III} \rightleftarrows Co^{II}$ (0.088 V) indicates the former to be more sensitive to electronic effects.

Acknowledgements

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