

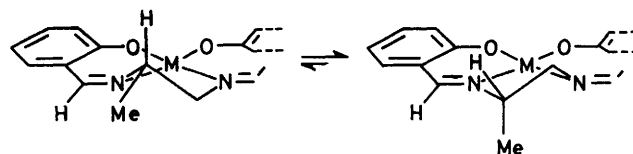
Structure and Electrochemical Properties of Bis(pyridine)cobalt(III) Complexes of *N,N'*-Ethylenebis(salicylideneimine) Homologues with an Aryl Substituent on the Ethylene Backbone. Crystal Structures of [Co(salpen)(py)₂]PF₆·0.5 Et₂O and [Co(salcppn)(py)₂]PF₆·2py (py = pyridine)†

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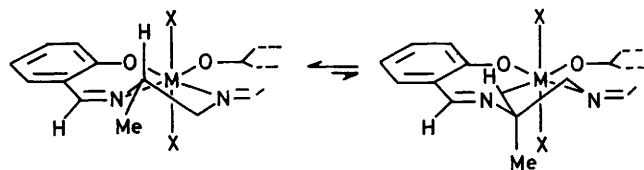
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Bis(pyridine)cobalt(III) complexes of salen homologues [$H_2\text{salen} = N,N'$ -ethylenebis(salicylideneimine)] with the substituent groups R^1 and R^2 on one of the ethylene carbon atoms, $[\text{Co}(\text{L})(\text{py})_2]\text{PF}_6$ ($\text{L} = \text{salen}$ homologue with $R^1 = \text{H}$ or Me , $R^2 = \text{aryl}$), have been synthesized and structurally characterized. Single-crystal X -ray analyses for $[\text{Co}(\text{salpen})(\text{py})_2]\text{PF}_6$ [$\text{salpen} = N,N'$ -1-phenylethylenebis(salicylideneimine)] and $[\text{Co}(\text{salcppn})(\text{py})_2]\text{PF}_6$ [$\text{salcppn} = N,N'$ -2-(*p*-chlorophenyl)propane-1,2-diylbis(salicylideneimine)] demonstrate six-co-ordination around the metal with pyridine molecules at the apical sites. The ethylene conformation is *gauche* for both complexes with the phenyl group in the equatorial orientation in the former and with the *p*-chlorophenyl group in the axial and the methyl group in the equatorial orientation in the latter. In $[\text{Co}(\text{salcppn})(\text{py})_2]\text{PF}_6$ the *p*-chlorophenyl group and one of the pyridine molecules are nearly parallel to each other so as to diminish the steric repulsion between them. The *gauche* conformation in solution is also deduced for the complexes in solution based on ^1H n.m.r. spectra. The $\text{Co}^{\text{III}}\text{--Co}^{\text{II}}$ reduction potentials of the complexes are not affected by mono-substitution on the ethylene carbon but significantly shifted to the positive side by disubstitution (aryl and methyl groups) on the ethylene carbon. The conformations and electrochemical properties of the complexes are discussed in terms of the steric interaction between the substituents (R^1 , R^2) and the pyridine molecule co-ordinated at the apical site.

It is known that planar metal complexes of salen homologues [$H_2\text{salen} = N,N'$ -ethylenebis(salicylideneimine)] with an alkyl substituent on the ethylene backbone prefer a *gauche* conformation with the substituent in the axial orientation (Scheme 1).^{1–5} This is attributed to a significant steric repulsion between the azomethine proton and the substituent in the equatorial orientation. For six-co-ordinate complexes with two donor groups at the apical sites, on the other hand, the preferred orientation of the substituent was shown to be equatorial, because of more severe steric repulsion between the substituent and the apical donor group¹ (Scheme 2). Therefore, the substituent(s) on the ethylene backbone often exerts a steric effect on binding or releasing molecules at the apical coordination sites.^{6–8} For example, in the case of bis(pyridine)cobalt(III) complexes of salen homologues, the methyl substituent(s) on the ethylene backbone facilitates the release of one of the pyridine molecules and thence the reduction to monopyridinecobalt(II) species.⁶ However, the effects of an aryl substituent on the conformation and physicochemical properties of the metal complexes have been less studied. Recently, we have suggested for bis(pyridine)copper(II) complexes of salen homologues with an alkyl and an aryl substituent on one of the ethylene carbons that the aryl group is axially oriented and stacked with the pyridine molecule co-ordinated at the apical site.⁹ In this study we have synthesized a series of bis(pyridine)cobalt(III) complexes of salen homologues with an aryl group on one of the ethylene carbons, and examined their structures and electrochemical properties in view of the intramolecular interaction between the substituent(s) and the pyridine



Scheme 1.



Scheme 2.

molecule. The chemical structure of the ligands is given in Figure 1, with the abbreviations used in this study.

Experimental

Syntheses.—Ethylenediamine and propane-1,2-diamine were purchased from Wako Chem. Co. Synthetic methods for the other diamines possessing one or two substituents on the ethylene carbon are described elsewhere.⁹ The ligands were obtained by condensing a diamine and salicylaldehyde in a 1:2 mole ratio. The compounds $[\text{Co}(\text{salen})(\text{py})_2]\text{PF}_6$ ¹⁰ and $[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6$ ⁹ (py = pyridine) were obtained by the literature methods. The other complexes were obtained as follows. A methanolic solution (40 cm³) containing the ligand (2×10^{-3} mol), cobalt(II) acetate tetrahydrate (2×10^{-3} mol), NaOH (2.5×10^{-3} mol), and pyridine (10 cm³) was stirred for 6 h under reflux in an open atmosphere. Then, an aqueous solution of KPF₆ (5×10^{-3} mol) was added, and the mixture was

[*N,N'*-1-Phenylethylenebis(salicylideneiminato)]bis(pyridine)cobalt(III) hexafluorophosphate-diethyl ether (2/1) and [*N,N'*-2-(*p*-chlorophenyl)propane-1,2-diylbis(salicylideneiminato)]bis(pyridine)cobalt(III) hexafluorophosphate-pyridine (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

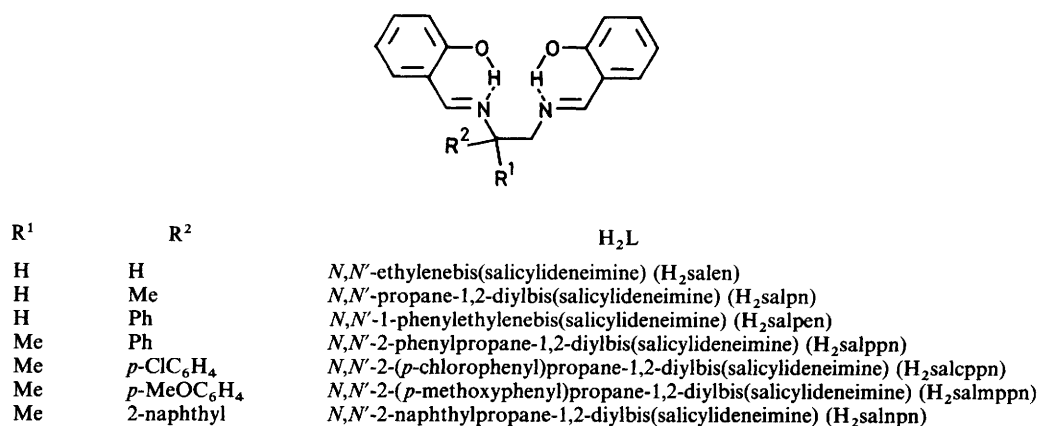
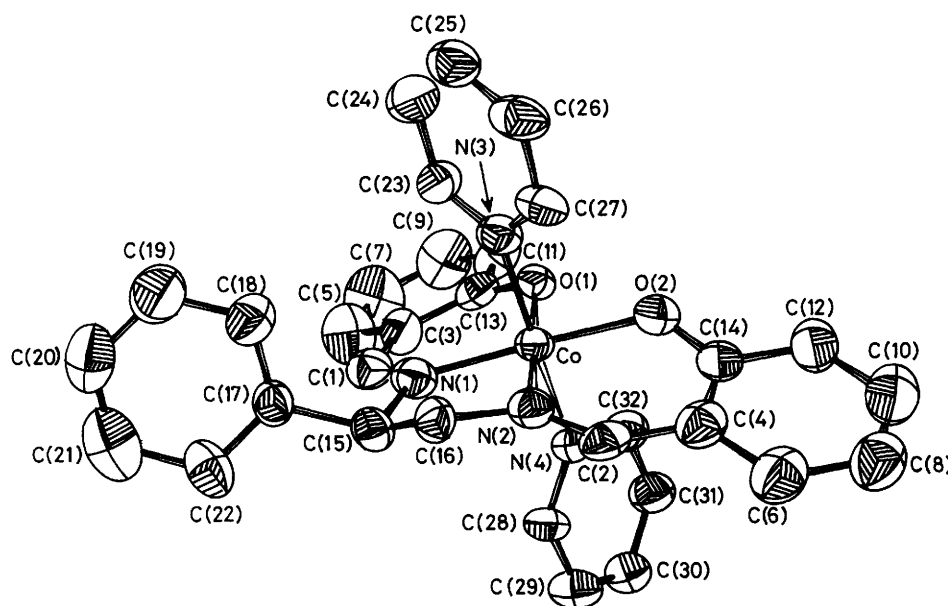


Figure 1. Chemical structure of the Schiff bases

Figure 2. Molecular structure of [Co(salen)(py)₂]⁺

refluxed for 3 h. The crude product, which separated on concentration of the solution, was thoroughly washed with water and then with diethyl ether, and crystallized from a pyridine–diethyl ether mixture.

The elemental analyses for the new [Co(L)(py)₂](PF₆) (L = salen homologue) complexes are given in Table 1.

Measurements.—Elemental analyses were obtained at the Elemental Analysis Service Center, Kyushu University. Hydrogen-1 n.m.r. spectra (90 MHz) were measured on a Hitachi R-20-B n.m.r. spectrometer in CDCl₃, using tetramethylsilane as the internal standard. Polarograms and differential pulse polarograms were measured on a model P-100 Yanagimoto voltammetric analyzer in dichloromethane containing tetrabutylammonium perchlorate (0.1 mol dm⁻³) as the supporting electrolyte. A three-electrode cell was used for the measurements, which was equipped with a glassy carbon working electrode, a platinum coil as the auxiliary electrode, and a calomel electrode as the reference electrode. The potentials were

normalized relative to the [Fe(η-C₅H₅)₂]⁺–[Fe(η-C₅H₅)₂]₂ potential^{11,12} as the internal standard.

X-Ray Crystal-structure Analyses.—Crystals of [Co(salen)(py)₂](PF₆)·0.5Et₂O (1) and [Co(salcppn)(py)₂](PF₆)·2py (2) suitable for X-ray study were obtained by recrystallization from a dilute pyridine–diethyl ether solution. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 73 Å) at 24 ± 1 °C.

Crystal data. For (1). C₃₄H₃₃CoF₆N₄O_{2.5}P, *M* = 741.56, triclinic, space group *P* $\bar{1}$, *a* = 14.112(4), *b* = 12.685(2), *c* = 10.525(4) Å, α = 97.37(3), β = 111.72(3), γ = 75.18(2)°, *Z* = 2, *D*_m = 1.12, *D*_c = 1.14 g cm⁻³, *F*(000) = 765, μ(Mo-K_α) = 5.1 cm⁻¹.

For (2). C₄₃H₄₀ClCoF₆N₆O₂P, *M* = 911.18, monoclinic, space group *P*2₁/*n*, *a* = 20.121(8), *b* = 12.715(3), *c* = 18.273(3) Å, β = 116.18(2)°, *Z* = 4, *D*_m = 1.44, *D*_c = 1.45 g cm⁻³, *F*(000) = 1 864, μ(Mo-K_α) = 6.1 cm⁻¹.

The intensity data were collected by the $2\theta-\omega$ scan technique ($3 < 2\theta < 55^\circ$) with a scan rate of 3° min^{-1} . The intensity data were corrected for Lorentz and polarization effects, but not for absorption. Independent, reflections, 4 159 for (1) and 3 765 for (2), with $|F_o| > 3\sigma(|F_o|)$ were used for the structure analysis.

The structures were solved by the direct method and refined by the block-diagonal least-squares method. Hydrogen atoms were not included in the refinement. Reliability factors were defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma w|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where $w = 1$. The final R factors for (1) and (2) were 0.059 and 0.071, respectively.

The atomic scattering factors were taken from International Tables.¹³ All calculations were carried out on the FACOM M-200 computer at the Computer Center of Kyushu University by the use of a local version¹⁴ of the UNICS-III¹⁵ and ORTEP¹⁶ programs. The final positional parameters with their estimated standard deviations are given in Tables 2 and 3.

Results and Discussion

In the crystals of (1) and (2) the anion PF_6^- and the solvated molecule [diethyl ether in (1) and pyridine in (2)] are separate from the complex cation, and it is presumed that these molecules do not affect the structure of the cation. Hence, our attention is focused only on the cation. Perspective diagrams

of the cations of (1) and (2) are given in Figures 2 and 3, respectively, together with the numbering system. Bond lengths and angles are given in Table 4.

Both complexes have a six-co-ordinate structure with the Schiff-base ligand in the equatorial plane and two pyridine molecules at the apical sites. The cobalt atom resides on the equatorial plane, and the Co-N(3) and Co-N(4) distances are

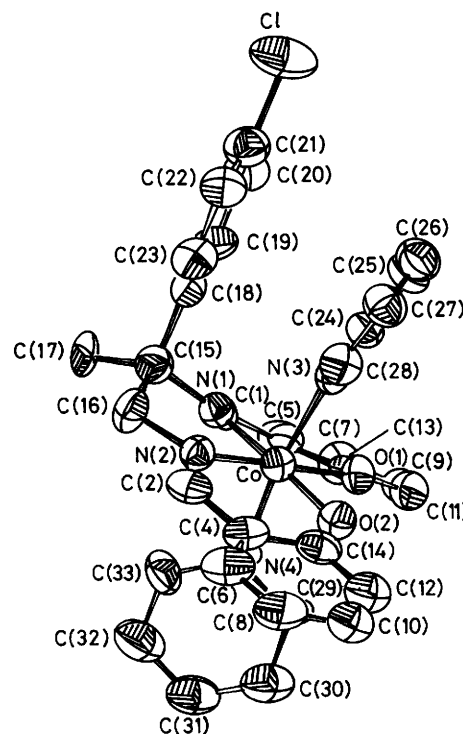


Figure 3. Molecular structure of $[\text{Co}(\text{salcppn})(\text{py})_2]^+$

Table 1. Elemental analyses of complexes

Complex	Found (%)			Calc. (%)		
	C	H	N	C	H	N
$[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6 \cdot \text{py}$	52.60	4.35	9.45	53.25	4.35	9.75
$[\text{Co}(\text{salpen})(\text{py})_2]\text{PF}_6 \cdot 0.5\text{Et}_2\text{O}$	55.00	4.60	7.50	55.05	4.50	7.55
$[\text{Co}(\text{salcppn})(\text{py})_2]\text{PF}_6$	55.25	4.30	8.10	55.15	4.20	7.80
$[\text{Co}(\text{salcppn})(\text{py})_2]\text{PF}_6$	52.80	4.20	7.75	52.65	3.90	7.45
$[\text{Co}(\text{salmppn})(\text{py})_2]\text{PF}_6$	54.75	4.45	7.65	54.55	4.30	7.50
$[\text{Co}(\text{salnpn})(\text{py})_2]\text{PF}_6 \cdot \text{py}$	59.90	4.60	8.20	59.50	4.40	8.25

Table 2. Fractional positional parameters ($\times 10^4$), with estimated standard deviations (e.s.d.s) in parentheses, for $[\text{Co}(\text{salpen})(\text{py})_2]\text{PF}_6 \cdot 0.5\text{Et}_2\text{O}$ (1)

Atom	x	y	z	Atom	x	y	z
Co	1 497(1)	2 076(1)	4 057(1)	N(3)	1 059(3)	692(4)	3 929(5)
O(1)	62(3)	2 764(3)	3 280(4)	C(23)	292(5)	441(5)	2 786(7)
O(2)	1 322(3)	2 401(3)	5 774(4)	C(24)	-70(5)	-515(6)	2 689(8)
N(1)	1 716(3)	1 757(4)	2 360(5)	C(25)	371(5)	-1 205(6)	3 774(8)
N(2)	2 918(3)	1 352(4)	4 809(5)	C(26)	1 166(5)	-953(5)	4 940(8)
C(1)	1 076(5)	2 162(5)	1 193(7)	C(27)	1 499(4)	9(5)	4 984(7)
C(2)	3 524(5)	1 429(5)	6 071(6)	N(4)	1 840(3)	3 514(4)	4 221(5)
C(3)	58(5)	2 854(5)	1 005(7)	C(28)	1 164(5)	4 399(5)	4 520(6)
C(4)	3 178(5)	2 038(5)	7 121(6)	C(29)	1 332(5)	5 447(5)	4 634(7)
C(5)	-517(7)	3 259(7)	-344(8)	C(30)	2 221(5)	5 606(5)	4 458(7)
C(6)	3 971(6)	2 141(6)	8 424(7)	C(31)	2 918(5)	4 684(5)	4 184(7)
C(7)	-1 534(7)	3 914(7)	-612(9)	C(32)	2 702(4)	3 664(5)	4 056(6)
C(8)	3 690(7)	2 682(7)	9 505(8)	P(1)	5 710(2)	2 309(3)	4 199(3)
C(9)	-1 972(6)	4 159(6)	395(8)	P(2)	5 770(4)	2 306(6)	4 417(7)
C(10)	2 633(7)	3 106(6)	9 331(8)	P(3)	5 668(5)	2 301(6)	4 018(7)
C(11)	-1 432(5)	3 783(6)	1 706(7)	F(1)	5 060(3)	2 039(4)	5 028(5)
C(12)	1 825(6)	3 026(6)	8 061(8)	F(2)	5 520(3)	3 539(3)	4 727(5)
C(13)	-392(4)	3 118(5)	2 032(6)	F(3)	6 364(4)	2 564(4)	3 388(5)
C(14)	2 101(5)	2 484(5)	6 933(7)	F(4)	6 751(3)	2 031(4)	5 523(5)
C(15)	2 797(4)	1 123(5)	2 444(7)	F(5)	4 664(3)	2 588(4)	2 922(5)
C(16)	3 304(4)	610(5)	3 830(6)	F(6)	5 923(4)	1 064(4)	3 700(5)
C(17)	2 786(5)	244(5)	1 292(6)	O(S)	5 381(9)	4 853(13)	9 960(16)
C(18)	2 266(6)	-568(6)	1 111(8)	C(S1)	5 278(21)	4 295(27)	7 693(27)
C(19)	2 303(7)	-1 387(7)	86(9)	C(S2)	4 998(27)	4 644(30)	8 423(39)
C(20)	2 850(6)	-1 361(7)	-751(8)	C(S3)	5 222(17)	5 112(18)	11 181(20)
C(21)	3 649(7)	-549(7)	-606(9)	C(S4)	5 693(24)	5 278(21)	12 283(25)
C(22)	3 349(6)	296(6)	466(8)				

Table 3. Fractional positional parameters ($\times 10^4$), with e.s.d.s in parentheses, for $[\text{Co}(\text{salcppn})(\text{py})_2]\text{PF}_6 \cdot 2\text{py}$ (2)

Atom	x	y	z	Atom	x	y	z
Co	4 816(1)	-68(1)	6 955(1)	C(25)	5 723(5)	2 693(7)	6 519(5)
O(1)	4 585(3)	-32(4)	5 833(3)	C(26)	6 449(5)	2 730(7)	7 144(6)
O(2)	5 621(3)	-929(4)	7 083(3)	C(27)	6 662(5)	1 963(7)	7 748(6)
N(1)	4 000(3)	786(4)	6 837(4)	C(28)	6 171(4)	1 173(6)	7 700(5)
N(2)	5 025(3)	-85(5)	8 073(3)	N(4)	4 206(3)	-1 356(5)	6 723(4)
C(1)	3 398(4)	917(6)	6 161(4)	C(29)	4 293(5)	-2 062(6)	6 212(5)
C(2)	5 507(4)	-681(6)	8 634(5)	C(30)	3 865(5)	-2 977(7)	5 980(6)
C(3)	3 330(4)	575(6)	5 382(4)	C(31)	3 354(5)	-3 177(7)	6 279(6)
C(4)	6 015(4)	-1 366(6)	8 508(5)	C(32)	3 279(6)	-2 471(8)	6 806(7)
C(5)	2 623(5)	748(7)	4 707(5)	C(33)	3 714(5)	-1 554(7)	7 026(6)
C(6)	6 508(5)	-1 963(7)	9 188(5)	Cl	5 454(2)	5 585(2)	7 812(2)
C(7)	2 529(5)	542(7)	3 927(5)	P	6 713(2)	1 092(2)	10 645(2)
C(8)	7 012(5)	-2 632(7)	9 111(6)	F(1)	6 811(4)	1 239(6)	11 533(4)
C(9)	3 125(5)	193(6)	3 786(5)	F(2)	6 588(5)	954(6)	9 736(3)
C(10)	7 063(5)	-1 452(6)	7 739(5)	F(3)	6 444(5)	-64(6)	10 642(4)
C(11)	3 821(5)	4(6)	4 431(4)	F(4)	7 047(5)	2 184(6)	10 676(5)
C(12)	6 593(4)	-2 125(6)	7 688(6)	F(5)	5 917(4)	1 491(9)	10 329(5)
C(13)	3 918(4)	173(5)	5 251(4)	F(6)	7 525(4)	648(7)	10 956(5)
C(14)	6 052(4)	-1 452(6)	7 739(5)	N(5)	4 100(11)	4 544(14)	4 026(12)
C(15)	4 069(5)	1 310(6)	7 622(4)	C(41)	4 200(8)	3 492(12)	4 296(10)
C(16)	4 515(5)	525(6)	8 303(5)	C(42)	3 746(7)	3 176(10)	4 560(7)
C(17)	3 308(4)	1 493(7)	7 627(5)	C(43)	3 273(8)	3 789(13)	4 671(7)
C(18)	4 460(4)	2 378(6)	7 685(5)	C(44)	3 211(8)	4 791(11)	4 436(11)
C(19)	5 135(5)	2 638(7)	8 341(5)	C(45)	3 654(11)	5 162(10)	4 167(14)
C(20)	5 438(5)	3 631(7)	8 376(5)	N(6)	3 941(11)	5 810(15)	8 857(11)
C(21)	5 079(5)	4 343(7)	7 761(6)	C(51)	4 097(15)	5 488(18)	9 592(11)
C(22)	4 397(5)	4 113(7)	7 082(6)	C(52)	3 893(13)	4 523(18)	9 782(10)
C(23)	4 099(5)	3 120(7)	7 072(5)	C(53)	3 525(11)	3 918(16)	9 196(10)
N(3)	5 470(3)	1 146(5)	7 089(3)	C(54)	3 305(9)	4 915(13)	8 452(10)
C(24)	5 250(5)	1 896(6)	6 505(5)	C(55)	3 516(9)	5 133(15)	8 226(9)

Table 4. Interatomic distances (Å) and bond angles ($^\circ$) in the co-ordination spheres of (1) and (2) with e.s.d.s in parentheses

	$[\text{Co}(\text{salpen})(\text{py})_2]^+$	$[\text{Co}(\text{salcppn})(\text{py})_2]^+$
Co-O(1)	1.894(1)	1.891(5)
Co-O(2)	1.905(6)	1.883(6)
Co-N(1)	1.907(6)	1.900(7)
Co-N(2)	1.891(1)	1.896(6)
Co-N(3)	1.987(2)	1.973(6)
Co-N(4)	1.992(1)	1.978(6)
O(1)-Co-O(2)	86.6(2)	86.4(2)
O(1)-Co-N(1)	95.2(2)	94.3(3)
O(2)-Co-N(2)	94.4(2)	95.1(3)
N(1)-Co-N(2)	84.1(2)	84.2(3)
N(3)-Co-O(1)	88.0(1)	87.0(3)
N(3)-Co-O(2)	89.4(3)	87.1(3)
N(3)-Co-N(1)	91.8(2)	93.6(3)
N(3)-Co-N(2)	90.7(1)	93.2(3)
N(3)-Co-N(4)	175.6(2)	172.8(3)
N(4)-Co-O(1)	88.5(1)	87.4(3)
N(4)-Co-O(2)	87.8(2)	95.1(3)
N(4)-Co-N(1)	91.1(3)	91.5(3)
N(4)-Co-N(2)	92.9(0)	92.4(3)

essentially the same (1.97–1.99 Å) in each case. These Co–N distances are close to the Co–N(n-butylamine) distance (1.99–2.01 Å) of $[\text{Co}(\text{salen})(\text{NH}_2\text{Bu}^n)_2]\text{PF}_6$ ¹⁷ and Co–N(pyridine) distance (2.03 Å) of $[\text{Co}(\text{salen})(\text{MeO})(\text{py})]$ ¹⁸ but considerably shorter than that of $[\text{Co}(\text{salen})(\text{py})]$ (2.14 Å).¹⁹ The average Co–O and Co–N distances in the equatorial plane (1.89 and 1.90 Å, respectively) are comparable to those of divalent and trivalent complexes with the salen ligand.²⁰

In the molecule of (1), the ethylene chain adopts a *gauche* conformation with the phenyl group in the equatorial orienta-

Table 5. Reduction potentials* (E/V vs. $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$ of the complexes

Complex	Co ^{III} –Co ^{II}	Co ^{II} –Co ^I
$[\text{Co}(\text{salen})(\text{py})_2]\text{PF}_6$	–0.90	–1.74
$[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6$	–0.91	–1.75
$[\text{Co}(\text{salpen})(\text{py})_2]\text{PF}_6$	–0.93	–1.75
$[\text{Co}(\text{salcppn})(\text{py})_2]\text{PF}_6$	–0.72	–1.74
$[\text{Co}(\text{salcppn})(\text{py})_2]\text{PF}_6$	–0.70	–1.74
$[\text{Co}(\text{salmppn})(\text{py})_2]\text{PF}_6$	–0.77	–1.75
$[\text{Co}(\text{salnnpn})(\text{py})_2]\text{PF}_6$	–0.74	–1.75

* Determined by d.p.p. in CH_2Cl_2 .

tion. The equatorial orientation of the phenyl group should result from the steric repulsion between the substituent and the pyridine molecule co-ordinated at the apical site, as pointed out previously¹ for $[\text{Co}(\text{salpn})(\text{py})\text{I}]$ and $[\text{Co}(\text{salpen})(\text{py})\text{I}]$. Both the pyridine molecules at the apical sites are essentially perpendicular to the least-square plane formed by Co, N(1), N(2), O(1), and O(2) (CoN_2O_2 plane).

The ethylene chain of (2) also adopts a *gauche* conformation with the methyl group in the equatorial orientation and the *p*-chlorophenyl group in the axial orientation. The *p*-chlorophenyl group and one of the pyridine molecules are oriented nearly parallel to each other, the dihedral angle being 15° and the average interplane distance *ca.* 3.5 Å. The Co–N(4) bond is nearly perpendicular to the CoN_2O_2 plane, whereas the Co–N(3) bond deviates considerably from perpendicularity to the plane, the angle formed by the Co–N bond and the plane being 78° . Thus, the pyridine molecule tilts away from the *p*-chlorophenyl group. This fact suggests that the interaction between the *p*-chlorophenyl group and the pyridine molecule is repulsive, in spite of the favourable interplanar distance (*ca.* 3.5 Å) for ring–ring stacking. Such a parallel orientation of the axial

aryl group and the co-ordinated pyridine molecule may diminish a steric repulsion between the rings and hence this conformer is energetically preferred to the other (*gauche* with axial methyl and equatorial aryl groups).

The ^1H n.m.r. spectrum of the $[\text{Co}(\text{L})(\text{py})_2]\text{PF}_6$ ($\text{L} = \text{salppn}$, salcpnp , salmppn , or salnnp) complexes showed an AB quartet near 4.8 p.p.m., attributable to the methylene proton signal. This fact indicates that the complexes maintain a *gauche* conformation with the axial aryl and the equatorial methyl groups, as demonstrated for $[\text{Co}(\text{salcpnp})(\text{py})_2]\text{PF}_6$ by single-crystal X -ray analysis. The complicated signals at 6.5–7.0 p.p.m. which are absent in the spectra of $[\text{Co}(\text{salen})(\text{py})_2]\text{PF}_6$ and $[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6$ are attributed to the protons of the aryl or pyridine rings in the 'stacked' orientation. The methyl signal of the complexes appears as a singlet at 2.1–2.2 p.p.m.

Each polarogram and differential pulse polarogram showed two reduction waves near -0.8 and -1.7 V (*vs.* $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$). The wave analysis for polarograms revealed both processes to be pseudo-reversible. For example, the slope of the $E_a - E$ *vs.* $\log[(i/i_a) - i]$ plot for $[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6$ is *ca.* 85 mV for the first reduction and 84 mV for the second reduction. Averill and Broman⁶ have shown that the reduction waves are attributable to the $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ and $\text{Co}^{\text{II}}\text{-Co}^{\text{I}}$ processes, respectively. The reduction potentials determined by differential pulse polarography (d.p.p.) are given in Table 5, together with the data for $[\text{Co}(\text{salen})(\text{py})_2]\text{PF}_6$ and $[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6$ obtained in this study. It is generally seen from Table 5 that mono-substitution on the ethylene backbone, irrespective of whether it is an alkyl or aryl group, does not affect the $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ potential, whereas di-substitution on the backbone markedly shifts the $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ potential to the positive side. On the other hand, the $\text{Co}^{\text{II}}\text{-Co}^{\text{I}}$ reduction potential is practically independent of the substitution on the ethylene backbone. We have already shown for $[\text{CuL}]^9$ that the substituents exert little electronic effect on the $\text{Cu}^{\text{II}}\text{-Cu}^{\text{I}}$ potential. Therefore, we presume that the positive shift of the $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ reduction potential on di-substitution is associated with a steric interaction between the substituted groups and the pyridine molecule co-ordinated at the apical site. Based on single-crystal X -ray analysis,¹⁹ e.s.r.,^{21,22} and kinetic²³ investigations, the cobalt(II) complexes of salen homologues have been revealed to form only monopyridine adducts. As pointed out by Hanzlik *et al.*,²⁴ one of the pyridine molecules must be released upon reduction of the bis(pyridine)cobalt(III) complexes on the electrode. In the case of $[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6$ and $[\text{Co}(\text{salpn})(\text{py})_2]\text{PF}_6$, the equatorially oriented group (Ph or Me) exerts practically no steric effect towards the pyridine molecules. This is reflected by their $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ reduction potentials, essentially the same as that of $[\text{Co}(\text{salen})(\text{py})_2]\text{PF}_6$. In the case of $[\text{Co}(\text{L})(\text{py})_2]\text{PF}_6$ ($\text{L} = \text{salppn}$, salcpnp , salmppn , or salnnp), however, one of the pyridine molecules is subject to

the steric effect from the axially oriented aryl group. Such steric interaction may tend to release the pyridine molecule and thence facilitate the reduction to the cobalt(II) species. In the case of $[\text{Co}(\text{L})(\text{py})_2]$ thus formed, there must be no steric interaction between the substituted groups (R^1 , R^2) and the pyridine molecule. Thus, it is understandable that the $\text{Co}^{\text{II}}\text{-Co}^{\text{I}}$ reduction potentials are practically independent of the substitution on the ethylene backbone.

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