Complexation of Cobalt(II) by the Hydrogenated Form of *N,N'*-*o*-Phenylenebis(salicylideneimine): the Crystal Structure of a Trinuclear Cobalt(II) Complex†

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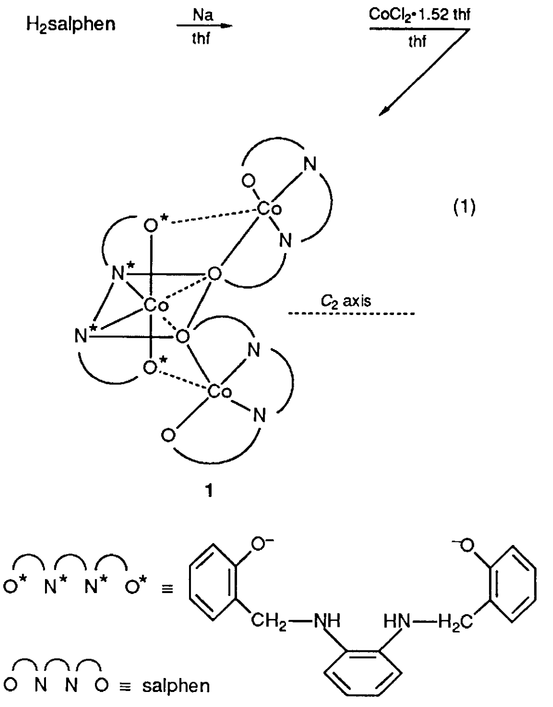
The reaction of *N,N'*-*o*-phenylenebis(salicylideneimine), H_2salphen, with sodium sand led to the hydrogenation of both imino groups of the ligand for $\frac{1}{3}$ of the amount of H_2salphen present. By adding $CoCl_2 \cdot 1.5$thf (thf = tetrahydrofuran) to the ligand mixture a trinuclear cobalt(II) complex **1** was isolated, and its structure determined. Crystallographic details: space group *C*2/*c* (monoclinic), a = 37.070(5), b = 14.036(2), c = 32.754(4) Å, β = 102.07(2)°, Z = 12 trimeric molecules, and R = 0.084 (R' = 0.095) for 7332 independent observed reflections with $I > 3\sigma(I)$.

Cobalt Schiff-base complexes have attracted a lot of attention because of their peculiar properties[1–3] and their reactivity mainly in the area of small molecule binding.[4,5] Synthetic methods for such complexes have usually been overlooked, mainly in non-aqueous solvents.[6]

A suitable method used in non-aqueous solvents is the reaction between the alkali-metal salt of the ligand and anhydrous metal halides. However, the generation of the sodium salt deserves some comments. During our studies on the synthesis of transition-metal Schiff-base complexes we have prepared alkali-metal salts from the free ligand and the corresponding hydrides,[6] or from the reaction with the alkali metal itself. The latter method led sometimes to unexpected results derived from the presence of hydrogenated forms of the ligand. The present report deals with the synthesis and the structural characterization of a trinuclear cobalt(II) complex derived from the fully hydrogenated form of *N,N'*-*o*-phenylenebis(salicylideneimine), H_2salphen.

Results and Discussion

The addition of sodium metal to a tetrahydrofuran (thf) solution of H_2salphen did not cause any appreciable evolution of H_2, while such evolution was observed when the reaction was carried out in benzene. In the latter solvent the expected Na_2(salphen) formed. The addition of $CoCl_2 \cdot 1.5$thf to the thf solution derived from the reaction of H_2salphen with an excess of sodium metal led to complex **1** (Scheme 1).



Scheme 1

In reaction (1) cobalt(II) adapts the ligand stoichiometry to form complex **1** regardless of the actual molar ratio between the hydrogenated and the intact form of salphen present in solution. The synthetic procedure might allow the elimination of other ligands or cobalt complexes, based on the solvent sequence used. The magnetic moment of 4.02 at 295 K per cobalt atom of **1** is in agreement with the values for cobalt(II) high-spin forms (see below).

The hydrogenation product, **1**, consists of cobalt salicylaldimine molecules which are associated into trimeric units. In each of the trimeric units there is one cobalt salicylaldimine molecule which has undergone hydrogenation. The complex crystallizes in the space group *C*2/*c* with twelve trimeric units per unit cell, four of which are on two-fold axes. Thus, the asymmetric unit consists of one trimer which has no associated symmetry and half of a second possessing a C_2 axis. Fig. 1, while showing the asymmetric unit, also shows the relative orientations of nearest-neighbour trimers; there are no significant contacts between these trimeric units. Fig. 2 provides more details of the asymmetric unit, and selected bond lengths and bond angles are in Table 1.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1** *

Co(1)–O(1)	1.965(6)	Co(1)–O(2)	2.041(6)	N(2)–C(13)	1.41(1)	N(2)–C(14)	1.30(1)
Co(1)–O(3)	2.015(5)	Co(1)–N(1)	2.111(9)	N(3)–C(27)	1.49(1)	N(3)–C(28)	1.46(1)
Co(1)–N(2)	2.051(7)	Co(2)–O(2)	2.098(5)	N(4)–C(33)	1.46(1)	N(4)–C(34)	1.51(1)
Co(2)–O(3)	2.138(6)	Co(2)–O(4)	2.116(6)	N(5)–C(53)	1.45(1)	N(5)–C(54)	1.27(1)
Co(2)–O(6)	2.112(5)	Co(2)–N(3)	2.094(6)	N(6)–C(47)	1.26(1)	N(6)–C(48)	1.43(1)
Co(2)–N(4)	2.118(7)	Co(3)–O(4)	1.999(5)	N(7)–C(67)	1.27(1)	N(7)–C(68)	1.43(1)
Co(3)–O(5)	1.944(6)	Co(3)–O(6)	2.056(6)	N(8)–C(73)	1.43(1)	N(8)–C(74)	1.28(1)
Co(3)–N(5)	2.083(8)	Co(3)–N(6)	2.058(8)	N(9)–C(87)	1.52(1)	N(9)–C(88)	1.46(1)
Co(4)–O(7)	1.943(5)	Co(4)–O(8)	2.052(6)	C(6)–C(7)	1.39(1)	C(14)–C(15)	1.43(1)
Co(4)–O(9)	2.009(5)	Co(4)–N(7)	2.115(8)	C(26)–C(27)	1.47(1)	C(34)–C(35)	1.52(2)
Co(4)–N(8)	2.027(7)	Co(5)–O(8)	2.060(5)	C(46)–C(47)	1.43(1)	C(54)–C(55)	1.41(1)
Co(5)–O(9)	2.146(6)	Co(5)–N(9)	2.104(6)	C(66)–C(67)	1.44(1)	C(74)–C(75)	1.44(1)
N(1)–C(7)	1.29(1)	N(1)–C(8)	1.39(1)	C(82)–C(87)	1.52(1)		
C(7)–N(1)–Co(1)	123.8(7)	C(8)–N(1)–Co(1)	111.4(6)	O(2)–Co(1)–O(1)	98.3(2)	O(3)–Co(1)–O(1)	99.5(2)
C(8)–N(1)–C(7)	124.6(9)	C(13)–N(2)–Co(1)	112.4(6)	O(3)–Co(1)–O(2)	83.7(2)	N(1)–Co(1)–O(1)	88.0(3)
C(14)–N(2)–Co(1)	125.3(7)	C(14)–N(2)–C(13)	122.2(8)	N(1)–Co(1)–O(3)	114.5(3)	N(2)–Co(1)–O(2)	87.8(3)
C(27)–N(3)–Co(2)	110.6(5)	C(28)–N(3)–Co(2)	109.6(5)	N(2)–Co(1)–O(3)	114.6(2)	N(2)–Co(1)–N(1)	76.4(3)
C(28)–N(3)–C(27)	113.2(7)	C(33)–N(4)–Co(2)	109.2(6)	O(3)–Co(2)–O(2)	79.4(2)	O(4)–Co(2)–O(2)	100.5(2)
C(34)–N(4)–Co(2)	108.2(6)	C(34)–N(4)–C(33)	116.4(8)	O(6)–Co(2)–O(2)	91.9(2)	O(6)–Co(2)–O(3)	103.9(2)
C(53)–N(5)–Co(3)	110.5(6)	C(54)–N(5)–Co(3)	126.0(7)	O(6)–Co(2)–O(4)	78.2(2)	N(3)–Co(2)–O(3)	90.1(3)
C(54)–N(5)–C(53)	122.1(9)	C(47)–N(6)–Co(3)	125.8(7)	N(3)–Co(2)–O(4)	89.9(3)	N(3)–Co(2)–O(6)	92.9(2)
C(48)–N(6)–Co(3)	110.9(6)	C(48)–N(6)–C(47)	122.7(8)	N(4)–Co(2)–O(2)	94.6(2)	N(4)–Co(2)–O(3)	90.7(3)
C(67)–N(7)–Co(4)	128.1(6)	C(68)–N(7)–Co(4)	110.4(5)	N(4)–Co(2)–O(4)	87.2(3)	N(4)–Co(2)–N(3)	83.1(3)
C(68)–N(7)–C(67)	120.9(8)	C(73)–N(8)–Co(4)	112.6(5)	O(5)–Co(3)–O(4)	102.2(2)	O(6)–Co(3)–O(4)	82.3(2)
C(74)–N(8)–Co(4)	127.2(6)	C(74)–N(8)–C(73)	119.7(7)	O(6)–Co(3)–O(5)	95.3(2)	N(5)–Co(3)–O(4)	115.9(3)
C(87)–N(9)–Co(5)	107.8(5)	C(88)–N(9)–Co(5)	109.3(5)	N(5)–Co(3)–O(5)	88.8(3)	N(6)–Co(3)–O(4)	115.7(2)
C(88)–N(9)–C(87)	116.2(7)			N(6)–Co(3)–O(6)	87.5(3)	N(6)–Co(3)–N(5)	77.6(3)
C(6)–C(7)–N(1)	129(1)	C(15)–C(14)–N(2)	127.6(9)	O(8)–Co(4)–O(7)	96.7(2)	O(9)–Co(4)–O(7)	102.0(2)
C(26)–C(27)–N(3)	113.3(7)	C(35)–C(34)–N(4)	112.6(8)	O(9)–Co(4)–O(8)	82.3(2)	N(7)–Co(4)–O(7)	87.0(2)
C(46)–C(47)–N(6)	124(1)	C(55)–C(54)–N(5)	126(1)	N(7)–Co(4)–O(9)	113.7(2)	N(8)–Co(4)–O(8)	88.1(3)
C(66)–C(67)–N(7)	124.1(9)	C(75)–C(74)–N(8)	125.4(8)	N(8)–Co(4)–O(9)	115.9(2)	N(8)–Co(4)–N(7)	78.7(3)
C(82)–C(87)–N(9)	109.7(7)			O(9)–Co(5)–O(8)	78.9(2)	N(9)–Co(5)–O(9)	88.9(2)
				O(8)–Co(5)–O(8′)	94.0(3)	N(9)–Co(5)–N(9′)	83.0(3)

* Primed atoms are related to their unprimed analogues by a C_2 axis.

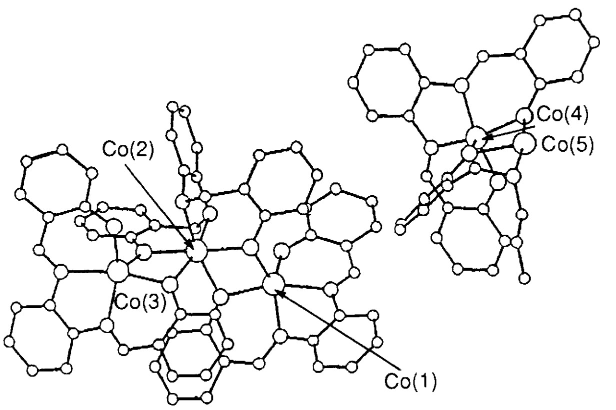

Fig. 1 The asymmetric unit of complex **1**, and a view of nearest-neighbour trimeric units

Table 2 Crystallographic data for complex **1** [a]

Cell contents	$C_{720}H_{552}Co_{36}N_{72}O_{80}$
Space group	$C2/c$ (monoclinic)
a/Å	37.070(5)
b/Å	14.036(2)
c/Å	32.754(4)
β/°	102.07(2)
U/Å^3	16 665 (71.3)
Z	12
D_c/g cm^{-3}	1.36
F(000)	6987.65
Crystal dimensions/mm	0.4 × 0.4 × 0.3
μ(Mo-Kα)/cm^{-1}	8.85
Data collected	$\pm h, +k, +l$
Unique reflections	12 652
Reflections with $I > 3\sigma(I)$	7332
R [b]	0.084
R' [c]	0.095
g	0.019 42
Maximum shift (e.s.d.)	0.001
Residual density (max., min.)/e Å^{-3}	0.45, −0.26
Goodness of fit [d]	0.92

[a] All measurements performed at 20 °C on a CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), scan range $2 < \theta < 24°$. [b] $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [c] $R' = \{[\Sigma w(|F_o - F_c|)^2]/[\Sigma w(|F_o|)^2]\}^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - gF_o{}^2]$. [d] Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

The trimeric units result from the fact that each phenolic oxygen of the central (hydrogenated) cobalt salicylaldimine molecule forms an intermolecular contact with the cobalt atom of a terminal Co(salphen), while a phenolic oxygen of each of the latter likewise forms an intermolecular contact with the central cobalt. The effect of these interactions is to produce two five-co-ordinated terminal cobalt(II) atoms and an octahedrally co-ordinated central cobalt. The octahedral geometry is produced by *cis* oxygen donor atoms, nitrogen atoms *trans* to these, and two further *trans* oxygen atoms, the latter nitrogen and oxygen atoms belonging to the hydrogenated salicylaldimine ligand. In the case of the trimer possessing two-fold axial symmetry, the axis passes through the octahedrally co-ordinated cobalt, Co(5), and bisects the N–Co–N bond angle. The analogous cobalt, Co(2), of the second trimeric unit has a very similar co-ordination geometry, which is only slightly relaxed from the demands of two-fold axial symmetry. The terminal cobalt atoms, Co(1), Co(3) and Co(4), display very similar five-co-ordinated geometries which are intermediate between trigonal bipyramidal and square pyramidal. The salicylaldimine ligands of the terminal cobalt and salicylaldimine

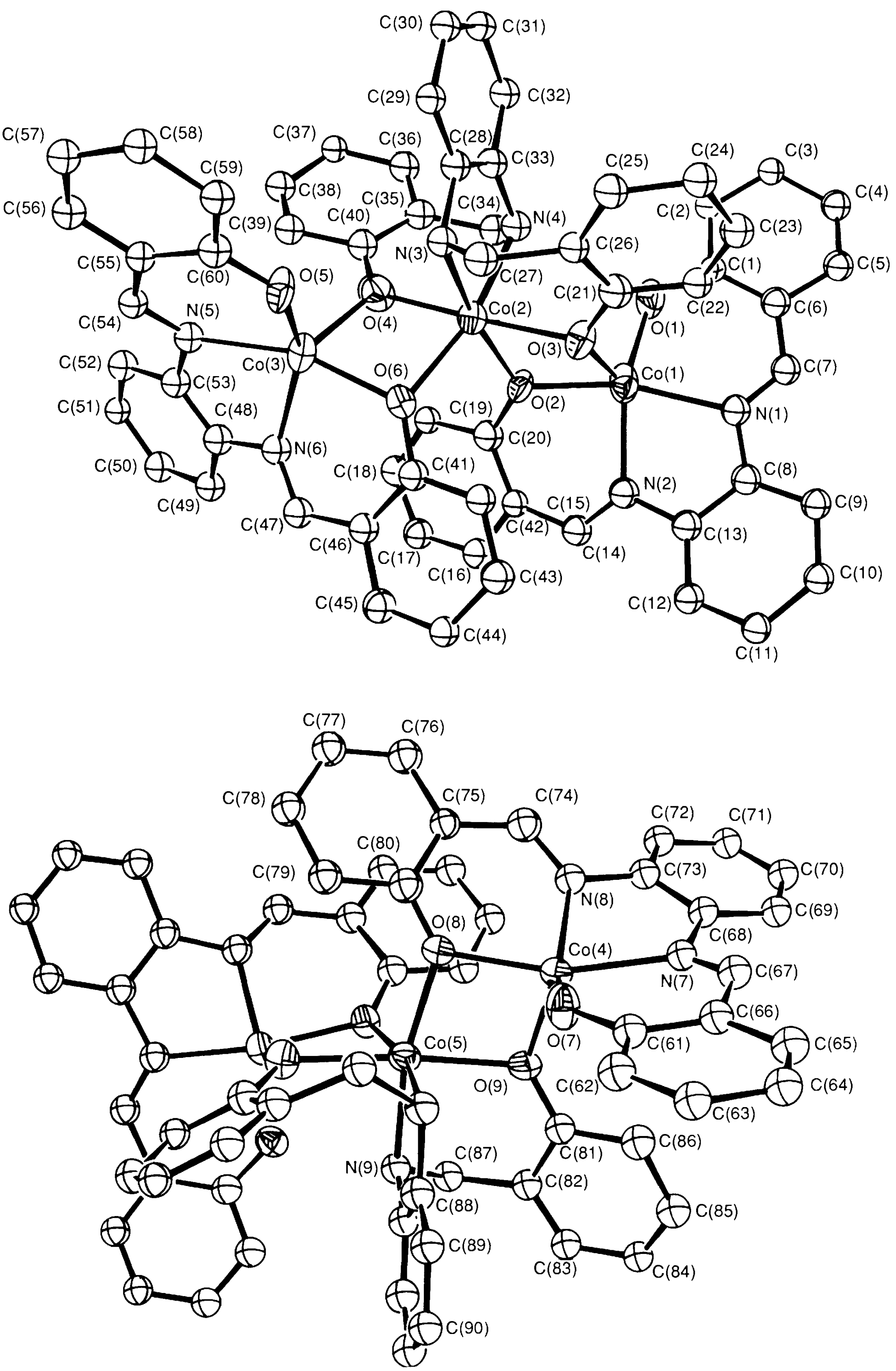

Fig. 2 A labelled asymmetric unit of complex **1**

molecules adopt an umbrella conformation, as is evident in Fig. 2 for Co(4)(salphen).[3]

The ranges of the intramolecular Co–O [1.943(5)–2.146(6) Å] and Co–N bond lengths [2.027(7)–2.118(7) Å] are somewhat wider than, though encompassing, those previously encountered for other high-spin cobalt(II) salicylaldimine complexes.[7] Several points are worth noting in respect to variations in the Co–O bond lengths. Since one phenolic oxygen of each terminal Co(salphen) is engaged in an intermolecular interaction, it forms a significantly longer intramolecular bond to the terminal

Table 3 Fractional atomic coordinates for complex **1** *

Atom	*x*	*y*	*z*
Co(1)	0.157 45(3)	0.150 32(9)	0.338 94(3)
Co(2)	0.153 24(3)	0.227 44(8)	0.426 46(3)
Co(3)	0.141 39(3)	0.167 42(8)	0.514 20(3)
O(1)	0.130 5(2)	0.260 7(5)	0.310 8(2)
O(2)	0.126 3(2)	0.128 0(4)	0.382 6(2)
O(3)	0.191 6(2)	0.217 8(4)	0.386 1(2)
O(4)	0.114 3(1)	0.240 9(4)	0.465 0(2)
O(5)	0.178 6(2)	0.258 3(4)	0.540 7(2)
O(6)	0.170 6(1)	0.119 8(4)	0.471 3(2)
Co(4)	0.420 83(3)	0.381 04(8)	0.255 42(3)
Co(5)	0.500 00	0.315 93(10)	0.250 00
O(7)	0.397 4(1)	0.283 4(4)	0.216 8(2)
O(8)	0.461 3(1)	0.416 0(4)	0.223 9(2)
O(9)	0.462 3(1)	0.308 4(4)	0.291 5(2)
N(1)	0.179 5(2)	0.129 2(5)	0.285 1(2)
N(2)	0.164 9(2)	0.005 7(5)	0.337 6(2)
N(3)	0.186 3(2)	0.331 0(5)	0.462 1(2)
N(4)	0.127 9(2)	0.347 6(5)	0.393 2(2)
N(5)	0.118 9(2)	0.171 7(5)	0.567 4(2)
N(6)	0.124 3(2)	0.029 1(5)	0.518 6(2)
C(1)	0.133 5(3)	0.304 9(7)	0.276 4(3)
C(2)	0.115 2(3)	0.391 4(9)	0.267 9(4)
C(3)	0.116 9(4)	0.443 2(11)	0.232 6(4)
C(4)	0.136 4(4)	0.405 3(10)	0.203 2(4)
C(5)	0.154 1(3)	0.324 0(7)	0.210 9(3)
C(6)	0.153 6(2)	0.270 3(7)	0.247 5(3)
C(7)	0.172 4(3)	0.183 9(7)	0.252 6(3)
C(8)	0.199 7(3)	0.045 4(7)	0.287 8(3)
C(9)	0.228 8(3)	0.028 5(8)	0.266 9(3)
C(10)	0.247 4(3)	−0.054 9(8)	0.273 6(4)
C(11)	0.241 3(3)	−0.121 4(9)	0.301 4(4)
C(12)	0.212 7(3)	−0.103 7(8)	0.324 0(3)
C(13)	0.193 2(3)	−0.020 1(7)	0.316 9(3)
C(14)	0.145 6(2)	−0.057 2(7)	0.352 6(3)
C(15)	0.118 1(2)	−0.040 5(6)	0.376 4(3)
C(16)	0.100 4(3)	−0.121 6(8)	0.387 1(3)
C(17)	0.073 8(3)	−0.113 7(8)	0.410 6(3)
C(18)	0.066 1(3)	−0.027 6(7)	0.424 2(3)
C(19)	0.082 8(2)	0.055 5(7)	0.414 0(3)
C(20)	0.109 4(2)	0.049 4(6)	0.391 1(3)
C(21)	0.215 3(2)	0.288 9(6)	0.381 7(3)
C(22)	0.224 4(3)	0.310 5(7)	0.344 6(3)
C(23)	0.248 5(3)	0.383 3(7)	0.340 6(3)
C(24)	0.264 1(3)	0.437 7(8)	0.373 3(3)
C(25)	0.254 9(3)	0.417 4(7)	0.411 7(3)
C(26)	0.231 5(2)	0.342 9(6)	0.416 7(3)
C(27)	0.225 4(3)	0.320 4(7)	0.458 4(3)
C(28)	0.171 3(3)	0.425 5(7)	0.450 3(3)
C(29)	0.186 3(3)	0.506 3(9)	0.472 0(4)
C(30)	0.171 5(4)	0.593 3(11)	0.459 3(4)
C(31)	0.143 5(4)	0.604 3(12)	0.428 3(5)
C(32)	0.127 3(4)	0.523 4(9)	0.405 5(4)
C(33)	0.142 0(3)	0.433 9(7)	0.415 5(3)
C(34)	0.086 7(3)	0.333 6(8)	0.384 9(4)
C(35)	0.071 0(3)	0.346 7(8)	0.423 8(3)
C(36)	0.040 5(4)	0.404 1(12)	0.420 7(5)
C(37)	0.019 9(7)	0.406 1(16)	0.453 3(7)
C(38)	0.036 9(8)	0.363 7(17)	0.488 3(10)
C(39)	0.068 5(4)	0.311 3(11)	0.494 4(5)
C(40)	0.085 6(3)	0.298 4(8)	0.461 8(3)
C(41)	0.181 9(2)	0.033 1(5)	0.467 4(2)
C(42)	0.208 2(2)	0.018 1(6)	0.443 0(3)
C(43)	0.222 9(3)	−0.069 8(7)	0.439 2(3)
C(44)	0.212 2(3)	−0.146 5(9)	0.460 2(4)
C(45)	0.185 9(3)	−0.137 2(9)	0.482 4(4)
C(46)	0.169 4(2)	−0.043 0(7)	0.486 8(3)
C(47)	0.140 4(3)	−0.044 3(7)	0.509 2(3)
C(48)	0.094 3(2)	0.024 7(6)	0.539 9(3)
C(49)	0.069 3(3)	−0.050 0(8)	0.535 8(4)
C(50)	0.040 6(3)	−0.042 8(9)	0.557 9(4)
C(51)	0.036 8(3)	0.034 0(9)	0.581 6(4)
C(52)	0.062 0(3)	0.104 9(8)	0.586 5(3)
C(53)	0.090 5(3)	0.099 7(7)	0.565 1(3)
C(54)	0.132 2(3)	0.216 0(7)	0.601 0(3)
C(55)	0.160 9(2)	0.283 7(6)	0.606 5(3)
C(56)	0.168 8(3)	0.334 3(7)	0.645 6(3)
C(57)	0.195 2(3)	0.400 3(7)	0.654 0(3)
C(58)	0.217 0(3)	0.416 6(8)	0.625 0(3)
C(59)	0.210 2(3)	0.368 6(7)	0.586 4(3)
C(60)	0.182 4(2)	0.301 2(6)	0.576 6(3)
N(7)	0.372 0(2)	0.383 5(5)	0.279 1(2)
N(8)	0.417 4(2)	0.521 1(5)	0.269 2(2)
N(9)	0.530 3(2)	0.203 7(5)	0.283 5(2)
C(61)	0.367 5(2)	0.230 5(6)	0.216 2(3)
C(62)	0.360 3(3)	0.155 8(7)	0.188 5(3)
C(63)	0.328 7(3)	0.098 1(8)	0.185 2(4)
C(64)	0.304 2(3)	0.115 0(7)	0.210 6(3)
C(65)	0.311 0(3)	0.186 8(7)	0.237 8(3)
C(66)	0.342 1(2)	0.247 7(6)	0.242 5(3)
C(67)	0.344 0(3)	0.329 9(6)	0.269 4(3)
C(68)	0.371 5(2)	0.465 3(6)	0.305 2(3)
C(69)	0.350 8(3)	0.474 9(7)	0.335 8(3)
C(70)	0.354 9(3)	0.556 5(7)	0.360 4(3)
C(71)	0.379 2(3)	0.622 0(8)	0.356 8(3)
C(72)	0.400 1(3)	0.616 7(7)	0.327 0(3)
C(73)	0.395 9(2)	0.537 6(6)	0.300 1(3)
C(74)	0.428 6(2)	0.591 8(6)	0.250 6(3)
C(75)	0.452 1(2)	0.585 6(6)	0.220 7(3)
C(76)	0.459 8(3)	0.673 2(7)	0.202 0(3)
C(77)	0.482 9(3)	0.678 0(7)	0.175 0(3)
C(78)	0.498 5(2)	0.595 6(6)	0.164 4(3)
C(79)	0.491 5(2)	0.507 0(6)	0.180 9(2)
C(80)	0.467 5(2)	0.500 3(6)	0.209 0(2)
C(81)	0.461 8(2)	0.237 5(5)	0.318 4(2)
C(82)	0.494 4(2)	0.193 3(6)	0.339 5(3)
C(83)	0.493 4(3)	0.124 8(8)	0.369 4(3)
C(84)	0.460 5(3)	0.094 9(8)	0.377 0(4)
C(85)	0.428 9(3)	0.130 7(7)	0.356 4(3)
C(86)	0.428 0(2)	0.204 3(6)	0.327 4(3)
C(87)	0.531 4(2)	0.220 0(7)	0.329 5(3)
C(88)	0.514 9(2)	0.113 1(6)	0.266 3(3)
C(89)	0.529 7(3)	0.029 0(8)	0.283 0(3)
C(90)	0.515 6(4)	−0.054 6(9)	0.266 9(4)
O(10)	0.197 20	0.243 38	0.087 71
O(11)	0.177 40	0.311 16	0.086 12
O(12)	0.147 68	0.357 48	0.072 49
O(13)	0.124 57	0.315 13	0.051 12

* Coordinates for O(10)–O(13) inclusive are those for the oxygen of the disordered water (see Experimental section).

cobalt than does the other phenolic oxygen of the same molecule. For example, the phenolic oxygens O(1) and O(2) form intramolecular bonds to the terminal cobalt Co(1), but O(2) is also engaged in an intermolecular interaction, and thus the Co(1)–O(1) and Co(1)–O(2) bond lengths are 1.965(6) and 2.041(6) Å, respectively. All of these intramolecular Co–O bond lengths [1.943(5)–2.056(6) Å] are shorter than the intramolecular bonds formed by the phenolic oxygens to the central cobalt atoms [2.116(6)–2.146(6) Å] and this is consistent both with the greater co-ordination of the central cobalt atoms and the fact that the phenolic oxygens of the central molecules make intermolecular Co–O contacts in the range 1.999(5)–2.015(5) Å whereas those on the terminal Co(salphen) molecules make contacts in the range 2.050(5)–2.112(5) Å.

From a chemical point of view the most significant aspect of the structure is that it demonstrates that only one third of the salicylaldimine molecules have undergone hydrogenation. Although hydrogen atoms were not detected, it is clearly evident from bond length and angle data that hydrogenation has occurred in some instances at the imine groups; it is this hydrogenation which has enabled the ligands to adopt the conformation they display about the octahedrally co-ordinated cobalt atoms. In the case of the terminal (non-hydrogenated) salicylaldimine ligands the imine C–N bond lengths vary within the range 1.25(1)–1.33(1) Å, whereas in the case of the central salicylaldimine ligands comparable bond lengths are within the range 1.49(1)–1.52(1) Å. The angle subtended at nitrogen by the carbon atom of the phenylene bridge and cobalt remains remarkably constant, being restricted to the range 108.8(6)–113.2(6)°. However, significant differences in bond angle data are apparent for other angles about the carbon and nitrogen atoms of the imine groups, these being reduced to the tetrahedral values (or approximately so) as a result of hydrogenation. For example, the C–N–Co, C–N–C and N–C–C bond angles fall within the ranges 122.4(7)–127.5(7), 120.6(8)–126(1) and 125(1)–129(1)° respectively for the non-hydrogenated ligands and these compare with the respective ranges 107.7(6)–110.8(6), 112.6(8)–116.6(8) and 109.6(7)–113.5(8)° for the hydrogenated ligands.

Experimental

The synthesis of H_2salphen was carried out by condensing, as usually, salicylaldehyde and *o*-phenylenediamine in ethanol. The compound $CoCl_2 \cdot 1.5$thf was obtained by a thf extraction of anhydrous $CoCl_2$. Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer and magnetic measurements were performed using a Faraday balance.

Synthesis of Complex **1**.—Sodium sand (2.50 g, 108.70 mmol) was added to a thf (500 cm^3) solution of H_2salphen (16.80 g, 52.80 mmol), then stirred. The colour changed from yellow to red-violet. The solution was refluxed and the excess of sodium and small amounts of some insoluble salts were filtered out. The compound $CoCl_2 \cdot 1.5$thf was added (12.57 g, 52.80 mmol) and the suspension refluxed for 30 min to give a red solution containing insoluble NaCl. The salt was filtered out and the solvent evaporated to dryness. The solid residue dissolved in 1,2-dimethoxyethane (250 cm^3) gave on standing red crystals of **1** (41%) (Found: C, 64.60; H, 4.75; N, 7.40. $C_{60}H_{46}Co_3N_6O_6$ requires C, 64.05; H, 4.10; N, 7.45%), μ_{eff} = 4.02 at 295 K per cobalt.

Crystal Structure Determination.—Crystallographic details are in Table 2. The structure was solved by direct methods, SHELX 86,[8] and refined by full-matrix least squares using SHELX 76.[9] Data were corrected for Lorentz and polarization effects but not for absorption. Cobalt and oxygen atoms (excluding the oxygen of the disordered water molecule) were refined anisotropically. Hydrogen atoms were included in calculated positions with fixed thermal parameters but no hydrogen atoms were included for the disordered water molecule. After inclusion and refinement of all atomic positions, there was residual electron density suggesting a disordered oxygen (of water) with approximately 0.25 site occupancy in each of four positions. In the final refinement this oxygen was included with fixed 0.25 site occupancy in each position. The atomic scattering factors for all atoms, and the anomalous dispersion correction factors for non-hydrogen atoms, were taken from the literature.[10–12] Final atomic coordinates are in Table 3. The PLUTO[13] and ORTEP[14] programs were used to produce the diagrams of Figs. 1 and 2 respectively.

Additional material available from the Cambridge Crystallographic Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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