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An unexpected chelate conformation in *trans*-[(*R*)-*N*,*N*′-bis(α-phenylsalicylidene)propane-1,2-diaminato(2−)]bis(1-methyl-1*H*-imidazole-κN^3)cobalt(III) perchlorate

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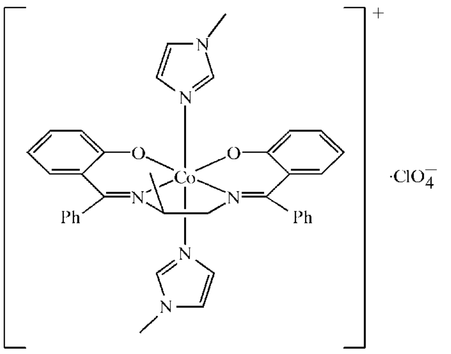
The title compound, $[Co(C_{29}H_{24}N_2O_2)(C_4H_6N_2)_2]ClO_4$, contains an optically active tetradentate Schiff base ligand in an equatorial plane and two 1-methylimidazole ligands at apical positions. The central N—C—C—N chelate ring of the Schiff base ligand has an envelope structure with a λ conformation, which is different from the solution structure predicted from circular dichroism and ^{1}H NMR spectra.

Comment

Cobalt(II) Schiff base complexes have been extensively utilized as catalysts for the oxidation reaction of organic molecules (Mukaiyama & Yamada, 1995; Fiammengo *et al.*, 2002). It has been recognized that the formal potential of the Co^{III}/Co^{II} couple is an important factor which determines the catalytic activity (Förster *et al.*, 1996). The redox potential of a Co^{II}– or Co^{III}–Schiff base complex is affected not only by the electronic effect, but also by the steric effect of the substituent on the Schiff base ligand (Kitaura *et al.*, 1987; Nishinaga *et al.*, 1991; Hirotsu *et al.*, 1994, 1996). In Co^{II} complexes with *N*,*N*′-bis(salicylidene)-1,2-ethanediamine derivatives, an axially oriented substituent on the central ethylene backbone affords a more positive value of the redox potential compared with a complex with an equatorially oriented substituent. This was rationally demonstrated by investigating the intramolecular steric interactions of related Co^{III}–Schiff base complexes with two apical ligands *L*, $[Co(\text{Schiff base})(L)_2]^+$ (Hirotsu *et al.*, 1996). For the title complex, (I), $[Co\{7\text{-Phsal-}(R)\text{-pn}\}(Meim)_2]ClO_4$ [$H_2\{7\text{-Phsal-}(R)\text{-pn}\}$ is (*R*)-*N*,*N*′-bis(α-phenylsalicylidene)-1,2-propanediamine and Meim is 1-methylimidazole], it has been reported that the central N···N chelate adopts the δ *gauche* conformation and the methyl group on the ethylene backbone is axially oriented, on the basis of circular dichroism and ^{1}H NMR spectra in acetonitrile solution. To clarify the intramolecular steric interactions, we have determined the single-crystal structure of (I) by X-ray analysis and present the results here.



(I)

The X-ray analysis of (I) confirmed the presence of a monovalent $[Co\{7\text{-Phsal-}(R)\text{-pn}\}(Meim)_2]^+$ complex cation and a perchlorate anion. The space group $P2_12_12_1$ is consistent with the fact that the complex has an optically active ligand derived from (*R*)-1,2-propanediamine. The absolute structure was chosen on the basis of the *R* configuration of the optically pure diamine employed.

In the complex cation, the Co^{III} ion is bound to two O and two N atoms of a Schiff base dianion, which form the equatorial plane. Two apical (ap) sites are occupied by N atoms of two 1-methylimidazole ligands, which complete the six-coordinate octahedral structure. The Co^{III} ion lies in the equatorial (eq) coordination plane with no significant deviation. The coordination bond distances are comparable with those in the related Co^{III} Schiff base complex with two 1-methylimidazole ligands, $[Co\{sal\text{-}(meso)\text{-stien}\}(Meim)_2]ClO_4$ [H_2sal-(*meso*)-stien is (*R*,*S*)-*N*,*N*′-bis(salicylidene)-1,2-diphenylethane-1,2-diamine; mean Co—O = 1.898 (4) Å, $Co—N_{eq}$ = 1.903 (4) Å and $Co—N_{ap}$ = 1.957 (4) Å; Hirotsu *et al.*, 1996].

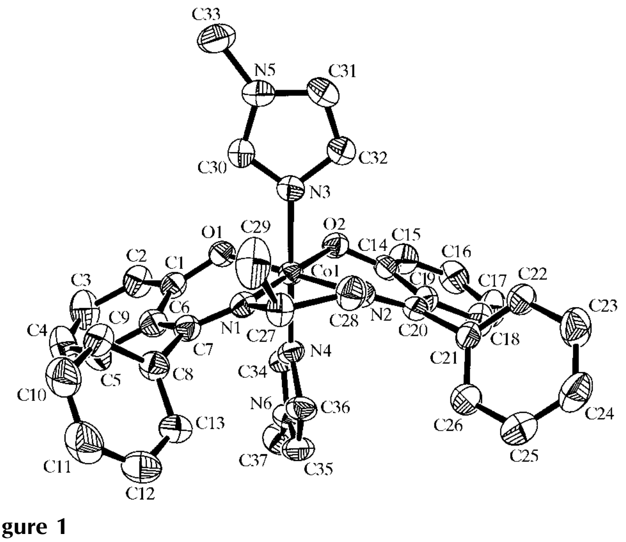


Figure 1
A view of the cation of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

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The central N···N chelate ring has an envelope-type structure with an N1—C27—C28—N2 torsion angle of −14.4 (5)°, which is much smaller than the corresponding angle in [Co{sal-(*meso*)-stien}(Meim)$_2$]$^+$ [42.5 (6)°]. The negative sign of this torsion angle in the cation of (I) is indicative of the λ conformation, which differs from the predominant solution structure containing the δ *gauche* conformation with the methyl group axially disposed. This suggests that the chelate conformation inverts rapidly in solution. The envelope structure and the δ *gauche* conformation are probably in equilibrium. A λ *gauche* conformation is unfavourable because of the steric repulsion between the equatorially disposed methyl group on the ethylene backbone and the phenyl group. The envelope structure may have a slightly higher energy than that of the δ *gauche* conformation, which largely contributes to the circular dichroism and ^{1}H NMR spectra in solution.

Experimental

The title complex was prepared according to the method previously reported by Hirotsu *et al.* (1996). Single crystals of (I) were obtained by slow evaporation of a dichloromethane–ethanol solution (1:2).

Crystal data

[Co($C_{29}H_{24}N_2O_2$)($C_4H_6N_2$)$_2$]ClO$_4$
M_r = 755.10
Orthorhombic, $P2_12_12_1$
a = 14.334 (2) Å
b = 17.766 (3) Å
c = 13.849 (2) Å
V = 3526.9 (9) Å^3
Z = 4
D_x = 1.422 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.7–15.0°
μ = 0.62 mm^{-1}
T = 298 (2) K
Prism, red
0.62 × 0.45 × 0.23 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.783, $T_{\max}$ = 0.867
6564 measured reflections
5671 independent reflections
4120 reflections with $F > 4\sigma(F)$
$R_{\rm int}$ = 0.012
$\theta_{\max}$ = 30.0°
$h = 0 \rightarrow 20$
$k = -12 \rightarrow 24$
$l = -10 \rightarrow 19$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.038
$wR(F^2)$ = 0.115
S = 1.04
5671 reflections
464 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.3625P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.007$
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.52 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0011
Absolute structure: Flack (1983)
Flack parameter = −0.01 (3)

The H atoms of the three methyl groups were refined as idealized CH$_3$ groups with a rotating motion. All other H atoms were placed in fixed positions by assuming C—H distances of 0.97 (CH$_2$), 0.98 (CH) or 0.93 Å (imidazole CH). All H atoms were treated as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The absolute structure was set by reference to the known chirality of the enantiopure diamine employed.

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.880 (3)	Co1—N2	1.889 (3)
Co1—O2	1.887 (3)	Co1—N3	1.950 (2)
Co1—N1	1.898 (3)	Co1—N4	1.927 (2)
O1—Co1—O2	87.3 (1)	O2—Co1—N4	89.3 (1)
O1—Co1—N1	93.6 (1)	N1—Co1—N2	85.8 (1)
O1—Co1—N2	179.4 (1)	N1—Co1—N3	92.5 (1)
O1—Co1—N3	88.8 (1)	N1—Co1—N4	90.0 (1)
O1—Co1—N4	89.9 (1)	N2—Co1—N3	91.3 (1)
O2—Co1—N1	178.8 (1)	N2—Co1—N4	90.0 (1)
O2—Co1—N2	93.3 (1)	N3—Co1—N4	177.25 (10)
O2—Co1—N3	88.3 (1)		
N1—C27—C28—N2	−14.4 (5)		

Data collection: *MSC/AFC Diffractometer Control Software* (MSC, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1186). Services for accessing these data are described at the back of the journal.

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