Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction:
ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{min} = 0.590$, $T_{max} = 0.719$
7131 measured reflections
7110 independent reflections
4835 reflections with $I > 2\sigma(I)$

$R_{int} = 0.007$
$\theta_{max} = 25°$
$h = -28 \rightarrow 28$
$k = -9 \rightarrow 0$
$l = -24 \rightarrow 24$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.091$
$S = 0.931$
7110 reflections
500 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.117$

$\Delta\rho_{max} = 0.476$ e Å^{-3}
$\Delta\rho_{min} = -0.439$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.597 (19)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N1	1.973 (6)	Cu2—N11	1.999 (5)
Cu1—N2	2.000 (6)	Cu2—N12	1.972 (6)
Cu1—N3	2.026 (5)	Cu3—N5	1.964 (6)
Cu1—N4	2.013 (5)	Cu3—N6	2.011 (5)
Cu2—N9	1.983 (5)	Cu3—N7	1.977 (4)
Cu2—N10	2.028 (6)	Cu3—N8	1.976 (6)
N1—Cu1—N2	112.5 (3)	N10—Cu2—N12	108.0 (2)
N1—Cu1—N3	112.3 (2)	N9—Cu2—N10	105.6 (2)
N1—Cu1—N4	109.9 (3)	N10—Cu2—N11	107.96 (19)
N2—Cu1—N3	106.7 (2)	N5—Cu3—N8	112.31 (17)
N2—Cu1—N4	105.4 (2)	N5—Cu3—N7	110.8 (3)
N3—Cu1—N4	109.8 (2)	N7—Cu3—N8	112.2 (3)
N9—Cu2—N12	110.7 (2)	N5—Cu3—N6	107.2 (3)
N11—Cu2—N12	113.4 (2)	N6—Cu3—N8	107.4 (3)
N9—Cu2—N11	110.8 (2)	N6—Cu3—N7	106.63 (19)

Methyl groups were refined as rigid groups allowed to rotate but not tip. However, slow convergence of some methyl parameters may indicate rotational disorder. The origin was fixed by the method of Flack & Schwarzenbach (1988). The structure was refined as a racemic twin with components 0.60 and 0.40 (2).

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1379). Services for accessing these data are described at the back of the journal.

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[*N*,*N*′-(1,1,2,2-Tetramethylethylene)bis(3,5-di-*tert*-butylsalicylideneiminato)]cobalt(II)†

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Abstract

Dimerization of the molecule of the title compound, $[Co(C_{36}H_{54}N_2O_2)]$, an efficient dioxygen carrier, is prevented by the methyl and *tert*-butyl substituents. The square-planar complex is bisected by a crystallographic mirror plane, with disorder of the $-CMe_2—CMe_2-$ region. Molecular dimensions [Co—O 1.846 (2) and Co—N 1.850 (2) Å] are very similar to those of the related 3-*tert*-butylsalicylidenato complex.

Comment

Transition metal Schiff base complexes are of interest in catalysis (Jacobsen *et al.*, 1991) and in small-molecule

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† Systematic name: {4,4′,6,6′-tetra-*tert*-butyl-2,2′-[1,1,2,2-tetramethylethanediylbis(nitrilomethylidyne)]diphenolato-*O*,*N*,*N*′,*O*′}cobalt(II).

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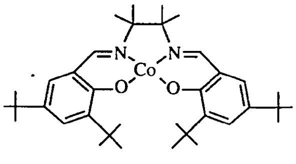
binding (Jones, Summerville & Basolo, 1979; Niederhoffer, Timmons & Martell, 1984; Chen & Martell, 1987). The title compound, (I), was investigated as part of a program to develop highly stable dioxygen carriers (Friesen *et al.*, 1993). The dioxygen adducts of Schiff base complexes of cobalt are often dimeric (Calligaris, Nardin & Randaccio, 1972; Avdeef & Schaefer, 1976), which limits their potential use in applications involving the binding of small molecules.



(I)

The X-ray structure of [Co(*t*-Bsaltmen)], where *t*-Bsaltmen = *N*,*N*′-(1,1,2,2,-tetramethylethylene)bis(3-*tert*-butylsalicylideneiminato), and in which a *tert*-butyl group lies *ortho* to each O atom, has been reported (Gall *et al.*, 1976). The title molecule has an additional *tert*-butyl group *para* to each O atom and is bisected by a crystallographic mirror plane, with disorder of the –CMe$_2$—CMe$_2$– region. Its structure and that of [Co(*t*-Bsaltmen)], including corresponding bond lengths and angles, are essentially identical, which would be expected because substitution *para* to oxygen does not introduce any further steric strain. The molecule is appreciably concave; the dihedral angle between the six-membered chelate rings is 3.3 (3)° and the angle between the phenyl rings is 14.1 (3)°. The molecules are not stacked, although the mean planes of two of the four molecules in the unit cell are parallel; these planes are sharply inclined to the planes of the other two molecules [dihedral angle 75.6 (3)°]. The shortest intermolecular distance between non-H atoms (C9···C18*A*) is 3.60 (1) Å. The additional *tert*-butyl groups were introduced to provide additional steric bulk and to increase solubility. The complex formed by the reaction of the title molecule with *p*-*N*,*N*-dimethylaminopyridine in *o*-dichlorobenzene reacts with dioxygen in a completely reversible manner over many cycles, indicating that the irreversible formation of a μ-peroxo dimer has been inhibited.

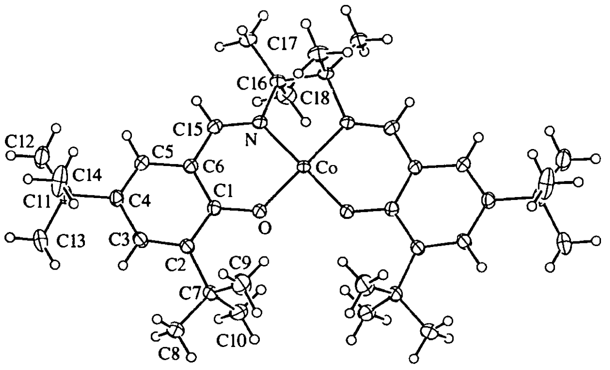


Fig. 1. An *ORTEP*II (Johnson, 1976) diagram (30% probability ellipsoids) showing the molecular structure and the atom-numbering scheme of (I). For clarity, only one of the two conformations in the –CMe$_2$—CMe$_2$– region is shown.

Experimental

The title compound was prepared under an argon atmosphere by dissolving the ligand (15.0 g, 0.027 mol) and [Co(O$_2$CCH$_3$)$_2$].4H$_2$O (7.5 g, 0.030 mol) in 600 ml methanol and refluxing for 1.5 h. Upon cooling the solution to ambient temperature, red crystals were deposited which were collected and dried on a glass frit. Yield: 13.9 g (85%). Elemental analysis for $C_{36}H_{54}CoN_2O_2$: calculated (found) C 71.37 (71.52), H 8.98 (9.17), N 4.62 (4.60), Co 9.73 (9.92)%. Mass spectroscopy: M^+, calculated (found) 606 (606). Deep-red crystals were grown from toluene and ethanol under argon. A crystal coated in epoxy was attached to a glass fiber.

Crystal data

[Co($C_{36}H_{54}N_2O_2$)]
$M_r = 605.77$
Orthorhombic
Pnma
$a = 11.1567\,(5)$ Å
$b = 25.439\,(2)$ Å
$c = 11.7631\,(6)$ Å
$V = 3338.5\,(8)$ Å^3
$Z = 4$
$D_x = 1.205$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 29.8$–$31.2°$
$\mu = 0.543$ mm^{-1}
$T = 294.2$ K
Tablet
0.38 × 0.31 × 0.25 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: azimuthal scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.85$, $T_{\max} = 0.87$
3323 measured reflections
3323 independent reflections

2378 reflections with $I > 1.5\sigma(I)$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 30$
$l = -13 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: −0.60%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.045$
$S = 2.33$
2378 reflections
206 parameters
H-atom parameters constrained
$w = 4F_o^2/[\sigma^2(I) + (0.02I)^2]$
$(\Delta/\sigma)_{\max} = 0.014$

$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: $I_o(\text{corr}) = I_o[1 + 2gI_c]$ (Stout & Jensen, 1968)
Extinction coefficient: $2.4\,(5) \times 10^{-7}$
Scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0.20374 (4)	1/4	0.53256 (4)	0.0268 (1)
O	0.2989 (2)	0.29958 (6)	0.4620 (2)	0.0340 (5)
N	0.1073 (2)	0.29949 (8)	0.6027 (2)	0.0346 (6)
C1	0.2893 (2)	0.35096 (9)	0.4597 (2)	0.0287 (7)
C2	0.3688 (2)	0.38138 (9)	0.3910 (2)	0.0300 (7)
C3	0.3497 (2)	0.43479 (10)	0.3857 (2)	0.0343 (7)
C4	0.2594 (2)	0.46228 (10)	0.4444 (2)	0.0330 (7)
C5	0.1881 (2)	0.43327 (10)	0.5134 (2)	0.0359 (8)
C6	0.1997 (2)	0.37770 (10)	0.5224 (2)	0.0316 (7)
C7	0.4689 (3)	0.35529 (10)	0.3222 (2)	0.0373 (8)
C8	0.5486 (3)	0.3951 (1)	0.2610 (3)	0.0545 (10)
C9	0.4117 (3)	0.3200 (1)	0.2309 (3)	0.062 (1)
C10	0.5500 (3)	0.3227 (1)	0.4000 (3)	0.057 (1)
C11	0.2418 (3)	0.52137 (10)	0.4236 (3)	0.0402 (8)
C12	0.1762 (3)	0.5479 (1)	0.5206 (3)	0.058 (1)
C13	0.3610 (4)	0.5493 (1)	0.4067 (4)	0.088 (1)
C14	0.1654 (4)	0.5282 (1)	0.3164 (3)	0.079 (1)
C15	0.1157 (3)	0.35043 (10)	0.5911 (3)	0.0402 (8)
C16*A*†	−0.0103 (6)	0.2751 (3)	0.6493 (5)	0.033 (2)
C16*B*†	0.0317 (6)	0.2787 (3)	0.6999 (6)	0.034 (2)
C17	−0.0698 (3)	0.3128 (1)	0.7349 (3)	0.0464 (9)
C18*A*†	−0.1003 (5)	0.2666 (2)	0.5519 (4)	0.045 (2)
C18*B*†	0.1077 (5)	0.2693 (2)	0.8056 (4)	0.043 (2)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Co—O	1.846 (2)	C5—C6	1.423 (4)
Co—N	1.850 (2)	C6—C15	1.419 (4)
O—C1	1.312 (3)	C7—C8	1.528 (4)
N—C15	1.306 (3)	C7—C9	1.538 (4)
N—C16*A*	1.552 (7)	C7—C10	1.530 (4)
N—C16*B*	1.517 (7)	C11—C12	1.515 (4)
C1—C2	1.428 (3)	C11—C13	1.521 (4)
C1—C6	1.416 (4)	C11—C14	1.532 (5)
C2—C3	1.377 (3)	C16*A*—C16*B*$^{\text{i}}$	1.563 (7)
C2—C7	1.530 (4)	C16*A*—C17	1.541 (7)
C3—C4	1.408 (4)	C16*A*—C18*A*	1.539 (8)
C4—C5	1.355 (4)	C16*B*—C17	1.485 (7)
C4—C11	1.536 (4)	C16*B*—C18*B*	1.524 (8)
O—Co—O$^{\text{i}}$	86.2 (1)	O—Co—N$^{\text{i}}$	179.55 (9)
O—Co—N	94.02 (8)	N—Co—N$^{\text{i}}$	85.8 (1)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

There was a centrosymmetric distribution of intensities. The structure was solved by heavy-atom methods in *Pnma*. Disorder in the central –CMe₂—CMe₂– section of the ligand, due to incompatibility of the ring puckering with the crystallographic mirror symmetry, gave alternative half-occupied positions for C16 and C18; alternative sites for C17 could not be distinguished. Structure solution in space-group $Pn2_1a$ showed the same disorder, with large correlation coefficients for refined corresponding parameters of pairs of atoms in the rest of the molecule. H atoms were included at updated riding positions [C—H 0.95 Å and $B(\text{H}) = 1.2B_{\text{eq}}(\text{C})$].

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Bis[2,3-butanedione dioximato(1−)-*N*,*N*′]-(pyridine){[(*R*)-5,6,7,8-tetrahydro-8-indolizinyl]methyl}cobalt(III)

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Abstract

The title compound, [Co($C_9H_{12}N$)($C_4H_7N_2O_2$)$_2$(C_5H_5-N)], has the expected structure with the C-bonded heterocyclic ligand *trans* to pyridine. The Co—C bond