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(*C*)-(2,4-Di-*tert*-butyl-6-{[(2*S*)-3,3-dimethyl-1-oxido-2-butyl]iminomethyl}phenolato)ethanol-*cis*-dioxomolybdenum(VI) at 100 K

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The central atom in the title complex, [Mo($C_{21}H_{32}NO_2$)O_2(C_2H_6O)], is offset from the equatorial plane of a tetragonally distorted octahedron. This plane is defined by three donor atoms from a tridentate Schiff base auxiliary (O_2N) and one oxo ligand. A second oxo ligand and an O donor atom of an ethanol molecule are located in axial positions of the coordination polyhedron. The absolute configuration at Mo is *C*. There are two molecules in the asymmetric unit.

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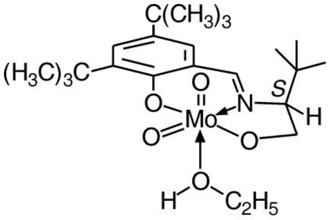
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.033
wR factor = 0.081
Data-to-parameter ratio = 19.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), was prepared in order to investigate its catalytic activity in oxidative cyclizations of alkenols (Hartung & Greb, 2002; Hartung *et al.*, 2006). The compound crystallizes as yellow prisms. Its identity was verified by X-ray diffraction at 100 K.



(I)

Compound (I) crystallizes in $P2_12_12_1$ (Z = 8). The asymmetric unit contains two molecules of (I) (hereafter complexes *A* and *B*; Figs. 1 and 2). Absolute structure determination was achieved using the Flack (1983) parameter, thus indicating an (*S*) configuration at the asymmetrically substituted C atom and *C* at Mo (Brown *et al.* 1975). The central atom is offset by 0.353 (1) Å from the equatorial plane of a tetragonally distorted octahedron that is defined by three donor atoms (O_2N) from the equatorially arranged tridentate Schiff base auxiliary, two *cis*-arranged oxo ligands, and the O atom of a coordinated ethanol molecule (Fig. 1). The distances between Mo and O atoms increase along the series Mo1—O1,2 (oxo O atoms) < Mo1—O3,4 (alkoxide O atoms) < Mo1—O5 (alcohol O atom) (Table 1). Based on reference values from the literature, the first set of *M*—O bonds is classified as double and the latter two sets as single bonds (Holm, 1987; Rao *et al.*, 1998; Sah *et al.*, 2001). Comparatively long connectivities, *i.e.* Mo1—O5 and Mo1—N1 (Table 1), are attributed to a low affinity of the associated neutral donor atoms toward the central atom (Reynolds *et al.*, 1984; Rehder, 1999). The observed bond lengths and angles in complex *B* are similar but not identical to those in *A* (Table 1). The most significant structural differences between the two complexes in the

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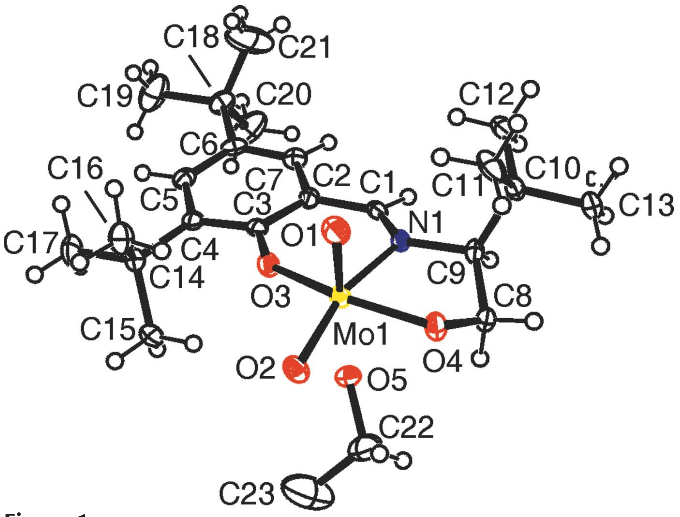

Figure 1
Molecular structure of complex *A*; O atoms are depicted in red, N atoms in blue and Mo atoms in yellow. Displacement ellipsoids are drawn at the 50% probability level.

asymmetric unit concern the chelate ring geometry (Fig. 3). The six-membered chelate ring in *A* adopts a twist-boat arrangement (Anet, 1987), with O3 and C2 offset in opposite directions from the Mo1/N1/C1/C3 mean plane [0.098 (4) Å for C2 and 0.062 (3) Å for O3]. In *B*, Mo2 is displaced by 0.778 (4) Å from the N2/C24/C25/C26/O8 mean plane, thus leading to a sofa conformation (Anet, 1987). The five-membered chelate rings adopt twist geometries (Fuchs, 1978), which are characterized by a displacement of C8 [0.339 (5) Å] and C9 [0.121 (5) Å] in opposite directions from the N1/Mo1/O4 plane in *A*, and by Mo2 [0.10 (1) Å] and O9 [0.634 (8) Å] from the N2/C32/C31 plane in *B*. The C22—C23 and C45—C46 distances appear unusually short for single Csp^3—Csp^3 bonds [1.473 (6) and 1.492 (7) Å] because of large displacement parameters in these fragments. The same explanation applies for the deviations of the Csp^3—Csp^3 distances from the corresponding mean value (Allen *et al.*, 1987) at one *tert*-butyl substituent.

Experimental

Compound (I) was prepared by heating a solution of (2*S*)-[bis-(2-methylprop-2-yl)]salicylidene-2-imine-3,3-dimethylbutanol (167 mg, 0.50 mmol) (Hartung *et al.*, 2006) and MoO_2Cl_2 (99.4 mg, 0.50 mmol) in EtOH (4 ml) for 30 min at 351 K. The solution was allowed to cool to 298 K and to stand at that temperature for 14 d to furnish yellow prisms, which were suitable for X-ray diffraction analysis.

Crystal data

$[Mo(C_{21}H_{32}NO_2)O_2(C_2H_6O)]$
$M_r = 504.48$
Orthorhombic, $P2_12_12_1$
$a = 11.5961\ (4)$ Å
$b = 19.9913\ (5)$ Å
$c = 23.2143\ (6)$ Å
$V = 5381.6\ (3)$ Å^3
$Z = 8$
$D_x = 1.245$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 14425 reflections
$\theta = 2.4$–29.5°
$\mu = 0.52$ mm^{-1}
$T = 100\ (2)$ K
Prism, yellow
0.40 × 0.36 × 0.32 mm

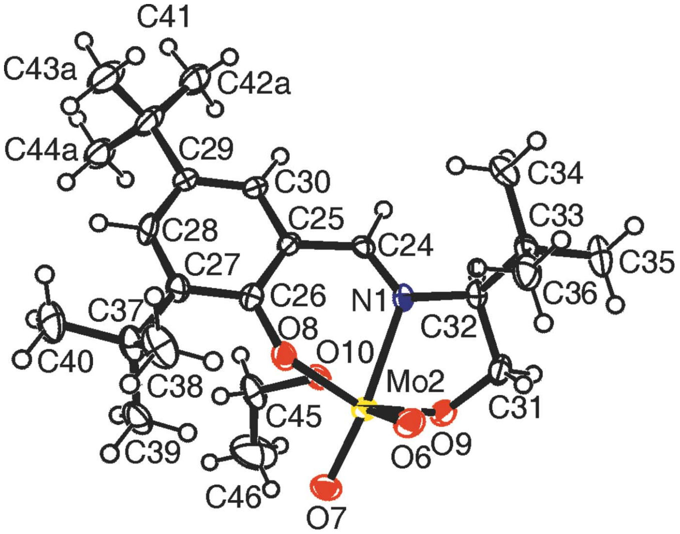

Figure 2
Molecular structure of complex *B*; O atoms are depicted in red, N atoms in blue and Mo atoms in yellow. Displacement ellipsoids are drawn at the 50% probability level.

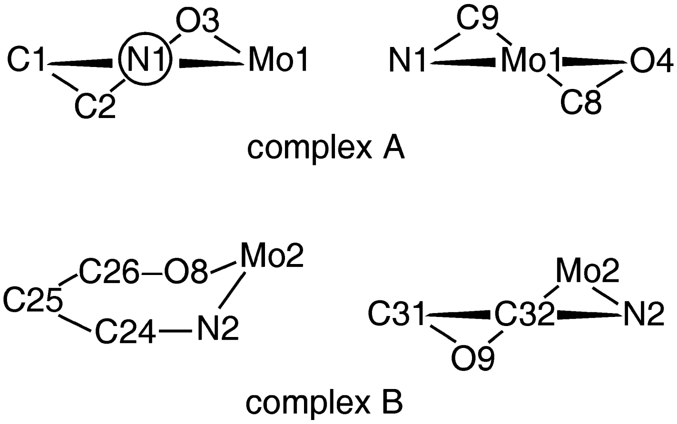

Figure 3
Chelate ring conformations of crystallographically independent complexes of (I). The circle (top left) symbolizes atom C3, which is located behind N1.

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector
ω scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2002)
$T_{min} = 0.829$, $T_{max} = 0.874$

35088 measured reflections
10881 independent reflections
10278 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 26.4°$
$h = -14 \rightarrow 8$
$k = -24 \rightarrow 24$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.081$
$S = 1.10$
10881 reflections
571 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 6.7957P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Absolute structure: Flack (1983), 4852 Friedel pairs
Flack parameter: −0.02 (3)

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.355 (4)	C32—C33	1.582 (5)
C1—C2	1.464 (4)	N1—Mo1	2.358 (3)
C2—C3	1.445 (4)	N2—Mo2	2.300 (3)
C8—O4	1.458 (4)	O1—Mo1	1.709 (2)
C8—C9	1.590 (5)	O2—Mo1	1.783 (2)
C9—N1	1.493 (4)	O3—Mo1	1.971 (2)
C9—C10	1.573 (4)	O4—Mo1	1.925 (2)
C24—N2	1.298 (4)	O5—Mo1	2.416 (2)
C24—C25	1.465 (5)	O6—Mo2	1.792 (3)
C25—C26	1.443 (5)	O7—Mo2	1.723 (2)
C31—O9	1.424 (4)	O8—Mo2	1.957 (2)
C31—C32	1.538 (5)	O9—Mo2	1.956 (3)
C32—N2	1.493 (4)	O10—Mo2	2.398 (2)
O1—Mo1—O2	102.43 (12)	O7—Mo2—O6	104.82 (12)
O1—Mo1—O4	98.34 (11)	O7—Mo2—O9	100.27 (12)
O2—Mo1—O4	98.05 (10)	O6—Mo2—O9	99.67 (11)
O1—Mo1—O3	99.67 (11)	O7—Mo2—O8	100.95 (11)
O2—Mo1—O3	100.83 (10)	O6—Mo2—O8	95.68 (11)
O4—Mo1—O3	150.35 (10)	O9—Mo2—O8	149.58 (10)
O1—Mo1—N1	100.63 (11)	O7—Mo2—N2	158.67 (11)
O2—Mo1—N1	156.87 (10)	O6—Mo2—N2	96.18 (11)
O4—Mo1—N1	76.77 (9)	O9—Mo2—N2	72.13 (10)
O3—Mo1—N1	76.89 (9)	O8—Mo2—N2	80.26 (10)
O1—Mo1—O5	175.56 (10)	O7—Mo2—O10	83.16 (10)
O2—Mo1—O5	81.87 (10)	O6—Mo2—O10	171.93 (10)
O4—Mo1—O5	82.02 (9)	O9—Mo2—O10	77.37 (9)
O3—Mo1—O5	78.28 (9)	O8—Mo2—O10	83.80 (9)
N1—Mo1—O5	75.11 (9)	N2—Mo2—O10	75.78 (9)

All H atoms were positioned geometrically and treated as riding atoms, with C—H distances in the range 0.95–1.00 Å and with $U_{\rm iso}$(H) set at $1.2U_{\rm eq}$ of the parent atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON2002* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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