metal-organic compounds

μ-Oxido-bis({4,4′-dibromo-2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}chromium(III))

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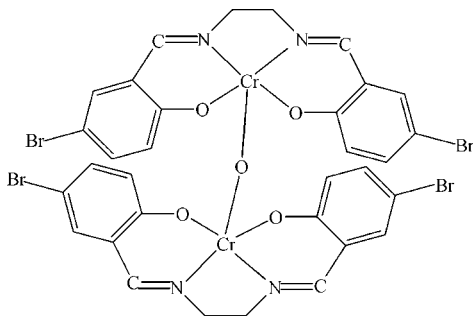Correspondence e-mail: yllctu@yahoo.com.cn

In the title compound, $[Cr_2(C_{16}H_{12}Br_2N_2O_2)_2O]$, Cr^{III} is chelated by a Schiff base ligand through two N and two O atoms, and is pentacoordinate, with a bridging oxide ion. The coordination geometry can be described as square-based pyramidal, with the bridging oxide in the apical site, giving the shortest bond. The bridging ligand lies on a crystallographic twofold rotation axis.

Related literature

For related literature, see: Chen *et al.* (2006); Garnovskii *et al.* (1993); Huang *et al.* (2002); Karacan *et al.* (2004).

Experimental

Crystal data

$[Cr_2(C_{16}H_{12}Br_2N_2O_2)_2O]$	V = 3488.3 (3) Å^3
M_r = 968.19	Z = 4
Orthorhombic, $Pcca$	Mo $K\alpha$ radiation
a = 21.1067 (10) Å	μ = 5.25 mm^{-1}
b = 13.3083 (10) Å	T = 293 (2) K
c = 12.4187 (5) Å	0.12 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	11021 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	3042 independent reflections
T_{min} = 0.572, T_{max} = 0.679	2168 reflections with $I > 2\sigma(I)$
	R_{int} = 0.117

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060	214 parameters
$wR(F^2)$ = 0.155	H-atom parameters not refined
S = 1.00	$\Delta\rho_{max}$ = 0.99 e Å^{-3}
3042 reflections	$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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supplementary materials

μ-Oxido-bis({4,4'-dibromo-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}chromium(III))

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Comment

The design of Schiff base complexes has attracted long-lasting research interest due to their important role in the development of coordination chemistry as well as inorganic biochemistry, catalysis, optical materials and so on (Garnovskii *et al.*, 1993; Huang *et al.*, 2002). Recently, Schiff base ligands, especially relatively flexible symmetrical or unsymmetrical Schiff base ligands and their hydrogenated derivatives, have been widely employed to assemble alkoxo- or phenoxo-bridged manganese clusters and polymers with novel topological structures and interesting magnetic, catalysis and photochemical properties (Chen *et al.*, 2006; Karacan *et al.*, 2004). In this paper, we report the structure of the title compound, (I).

As shown in Fig. 1, Cr^{III} is chelated by the Schiff base ligand through two N and two O atoms. The chromium(III) ion is pentacoordinate with three oxygen atoms and two nitrogen atoms from the Schiff base ligand and a bridging oxide ion. The coordination geometry can be described as square-based pyramidal, with the bridging oxide in the apical site, giving the shortest bond. The bridging ligand lies on a crystallographic twofold rotation axis.

Experimental

A mixture of chromium(III) acetylacetonate (1 mmol, 0.35 g) and 4,4'-dibromo-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenol (1 mmol, 0.45 g) in 20 ml me thanol was refluxed for two hours. The cooled solution was filtered and the filtrate was allowed to evaporate at room temperature. Several days later, blue blocks of (I) were obtained in a yield of 21%. Anal. Calc. for $C_{32}H_{24}Br_4Cr_2N_4O_5$: C 39.67, H 2.48, N 5.79%; Found: C 39.61, H 2.49, N 5.75%.

Refinement

All H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 Å (sp^2), and 0.97%A (sp^3) and $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(C)$.
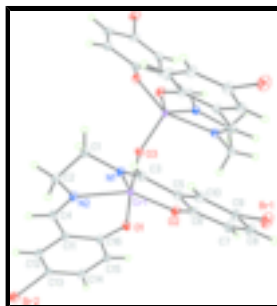
Figures

Fig. 1. The molecular structure of (I), drawn with 30% probability displacement ellipsoids for the non-hydrogen atoms. [Symmetry code for unlabelled atoms: $-x, y, 1/2 - z$.]

supplementary materials

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Crystal data

$[Cr_2(C_{16}H_{12}Br_2N_2O_2)_2O]$	$F_{000} = 1888$
$M_r = 968.19$	$D_x = 1.844$ Mg m^{-3}
Orthorhombic, *Pcca*	Mo *Kα* radiation $λ = 0.71073$ Å
Hall symbol: -P 2a 2ac	Cell parameters from 3073 reflections
$a = 21.1067\ (10)$ Å	$θ = 3.0–25.1º$
$b = 13.3083\ (10)$ Å	$μ = 5.25$ mm^{-1}
$c = 12.4187\ (5)$ Å	$T = 293\ (2)$ K
$V = 3488.3\ (3)$ Å^3	Block, blue
$Z = 4$	$0.12 × 0.10 × 0.08$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	3042 independent reflections
Radiation source: fine-focus sealed tube	2168 reflections with $I > 2σ(I)$
Monochromator: graphite	$R_{int} = 0.117$
$T = 293(2)$ K	$θ_{max} = 25.1º$
φ and ω scans	$θ_{min} = 3.0º$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = −25→25$
$T_{min} = 0.572$, $T_{max} = 0.679$	$k = −15→15$
11021 measured reflections	$l = 0→14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2σ(F^2)] = 0.060$	H-atom parameters not refined
$wR(F^2) = 0.155$	$w = 1/[σ^2(F_o^2) + (0.086P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(Δ/σ)_{max} < 0.001$
3042 reflections	$Δρ_{max} = 0.99$ e Å^{-3}
214 parameters	$Δρ_{min} = −0.75$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, convention-al R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cr1	0.07193 (4)	0.12984 (5)	0.31472 (6)	0.0285 (3)
Br2	0.28253 (4)	−0.28112 (6)	0.48703 (7)	0.0693 (3)
Br1	0.10796 (4)	0.66037 (5)	0.24484 (7)	0.0820 (4)
C16	0.1642 (3)	−0.0344 (4)	0.3175 (4)	0.0388 (12)
C15	0.2037 (3)	−0.0951 (4)	0.2516 (5)	0.0451 (14)
H15	0.2059	−0.0854	0.1775	0.054*
C14	0.2376 (3)	−0.1671 (4)	0.3006 (5)	0.0508 (16)
H14	0.2657	−0.2059	0.2608	0.061*
C13	0.2305 (3)	−0.1852 (4)	0.4171 (5)	0.0471 (15)
C12	0.1905 (3)	−0.1316 (4)	0.4828 (5)	0.0455 (15)
H12	0.1868	−0.1452	0.5559	0.055*
C11	0.1560 (3)	−0.0555 (4)	0.4328 (5)	0.0398 (13)
C4	0.1148 (3)	−0.0005 (4)	0.5090 (4)	0.0403 (13)
H4	0.1150	−0.0191	0.5812	0.048*
C2	0.0463 (3)	0.1212 (4)	0.5716 (5)	0.0459 (14)
H2A	0.0231	0.0725	0.6143	0.055*
H2B	0.0765	0.1554	0.6176	0.055*
C1	0.0011 (3)	0.1961 (5)	0.5201 (5)	0.0464 (15)
H1A	−0.0380	0.1631	0.4992	0.056*
H1B	−0.0089	0.2498	0.5702	0.056*
C3	0.0406 (3)	0.3283 (4)	0.4142 (5)	0.0432 (14)
H3	0.0242	0.3697	0.4676	0.052*
C5	0.0737 (3)	0.3750 (4)	0.3201 (5)	0.0419 (13)
C10	0.0742 (3)	0.4751 (4)	0.3226 (5)	0.0504 (15)
H10	0.0556	0.5103	0.3790	0.061*
C9	0.1039 (3)	0.5252 (5)	0.2371 (6)	0.0560 (17)
C8	0.1315 (3)	0.4779 (5)	0.1450 (6)	0.0587 (18)
H8	0.1497	0.5155	0.0899	0.070*
C7	0.1302 (3)	0.3797 (5)	0.1412 (5)	0.0548 (16)
H7	0.1466	0.3455	0.0821	0.066*
C6	0.1030 (3)	0.3258 (4)	0.2299 (5)	0.0444 (14)
N2	0.0797 (2)	0.0704 (3)	0.4795 (4)	0.0399 (11)
N1	0.0344 (2)	0.2372 (3)	0.4230 (4)	0.0393 (11)
O3	0.0000	0.0842 (4)	0.2500	0.0404 (13)
O1	0.1370 (2)	0.0412 (3)	0.2689 (3)	0.0443 (10)
O2	0.10570 (19)	0.2323 (3)	0.2222 (3)	0.0470 (10)

supplementary materials

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.0374 (5)	0.0172 (4)	0.0310 (4)	0.0006 (3)	0.0006 (4)	−0.0001 (3)
Br2	0.0685 (5)	0.0550 (5)	0.0845 (6)	0.0219 (3)	0.0092 (4)	0.0254 (4)
Br1	0.1113 (8)	0.0274 (4)	0.1074 (7)	−0.0027 (3)	0.0294 (5)	0.0094 (4)
C16	0.046 (3)	0.026 (3)	0.044 (3)	−0.002 (2)	0.003 (3)	0.000 (2)
C15	0.054 (4)	0.032 (3)	0.049 (3)	0.004 (3)	0.001 (3)	0.001 (3)
C14	0.051 (4)	0.033 (3)	0.068 (4)	0.005 (3)	0.008 (3)	0.004 (3)
C13	0.044 (3)	0.037 (3)	0.061 (4)	0.006 (3)	0.008 (3)	0.015 (3)
C12	0.052 (4)	0.035 (3)	0.050 (3)	0.000 (3)	0.000 (3)	0.011 (3)
C11	0.044 (3)	0.029 (3)	0.047 (3)	0.000 (2)	−0.003 (3)	0.003 (2)
C4	0.054 (4)	0.027 (3)	0.041 (3)	−0.003 (3)	−0.003 (3)	0.002 (2)
C2	0.055 (4)	0.036 (3)	0.046 (3)	−0.002 (3)	0.010 (3)	−0.001 (3)
C1	0.054 (4)	0.035 (3)	0.050 (4)	−0.001 (3)	0.011 (3)	0.004 (3)
C3	0.046 (4)	0.035 (3)	0.048 (3)	0.002 (2)	0.000 (3)	−0.005 (3)
C5	0.046 (3)	0.026 (3)	0.053 (3)	0.000 (2)	0.000 (3)	0.003 (3)
C10	0.052 (4)	0.032 (3)	0.068 (4)	0.001 (3)	0.006 (3)	0.000 (3)
C9	0.064 (4)	0.028 (3)	0.076 (4)	0.000 (3)	0.009 (4)	0.015 (3)
C8	0.069 (5)	0.034 (3)	0.073 (4)	−0.004 (3)	0.010 (4)	0.007 (3)
C7	0.068 (4)	0.039 (3)	0.058 (4)	−0.002 (3)	0.010 (3)	0.010 (3)
C6	0.044 (4)	0.031 (3)	0.058 (4)	−0.001 (2)	0.005 (3)	0.001 (3)
N2	0.049 (3)	0.028 (2)	0.042 (3)	0.001 (2)	0.002 (2)	−0.002 (2)
N1	0.045 (3)	0.023 (2)	0.049 (3)	−0.0050 (19)	0.006 (2)	0.002 (2)
O3	0.045 (3)	0.025 (3)	0.052 (3)	0.000	−0.008 (3)	0.000
O1	0.059 (3)	0.030 (2)	0.044 (2)	0.0110 (18)	−0.0010 (19)	0.0033 (17)
O2	0.059 (3)	0.028 (2)	0.054 (2)	−0.0008 (17)	0.012 (2)	0.0030 (18)

Geometric parameters (Å, °)

Cr1—O3	1.8220 (19)	C2—N2	1.503 (7)
Cr1—O1	1.897 (4)	C2—H2A	0.970
Cr1—O2	1.920 (4)	C2—H2B	0.970
Cr1—N1	2.116 (5)	C1—N1	1.499 (8)
Cr1—N2	2.200 (5)	C1—H1A	0.970
Br2—C13	1.894 (6)	C1—H1B	0.970
Br1—C9	1.803 (6)	C3—N1	1.224 (7)
C16—O1	1.307 (6)	C3—C5	1.497 (8)
C16—C15	1.420 (8)	C3—H3	0.930
C16—C11	1.470 (8)	C5—C10	1.332 (8)
C15—C14	1.342 (8)	C5—C6	1.437 (8)
C15—H15	0.930	C10—C9	1.402 (9)
C14—C13	1.474 (9)	C10—H10	0.930
C14—H14	0.930	C9—C8	1.431 (9)
C13—C12	1.373 (9)	C8—C7	1.308 (8)
C12—C11	1.394 (8)	C8—H8	0.930
C12—H12	0.930	C7—C6	1.434 (8)
C11—C4	1.478 (8)	C7—H7	0.930

C4—N2	1.255 (7)	C6—O2	1.250 (7)
C4—H4	0.930	O3—Cr1[i]	1.8220 (19)
C2—C1	1.521 (9)		
O3—Cr1—O1	105.27 (18)	N1—C1—C2	106.4 (5)
O3—Cr1—O2	106.37 (17)	N1—C1—H1A	110.4
O1—Cr1—O2	89.60 (17)	C2—C1—H1A	110.4
O3—Cr1—N1	101.15 (16)	N1—C1—H1B	110.5
O1—Cr1—N1	151.81 (18)	C2—C1—H1B	110.5
O2—Cr1—N1	92.28 (17)	H1A—C1—H1B	108.6
O3—Cr1—N2	110.63 (15)	N1—C3—C5	122.1 (5)
O1—Cr1—N2	90.13 (17)	N1—C3—H3	119.0
O2—Cr1—N2	141.66 (19)	C5—C3—H3	119.0
N1—Cr1—N2	71.29 (17)	C10—C5—C6	118.0 (6)
O1—C16—C15	115.5 (5)	C10—C5—C3	113.6 (6)
O1—C16—C11	123.0 (5)	C6—C5—C3	128.3 (5)
C15—C16—C11	121.5 (5)	C5—C10—C9	117.5 (6)
C14—C15—C16	117.2 (6)	C5—C10—H10	121.2
C14—C15—H15	121.4	C9—C10—H10	121.2
C16—C15—H15	121.4	C10—C9—C8	125.3 (6)
C15—C14—C13	120.6 (6)	C10—C9—Br1	117.1 (5)
C15—C14—H14	119.7	C8—C9—Br1	117.5 (5)
C13—C14—H14	119.7	C7—C8—C9	117.4 (6)
C12—C13—C14	124.0 (5)	C7—C8—H8	121.3
C12—C13—Br2	115.7 (4)	C9—C8—H8	121.3
C14—C13—Br2	120.1 (4)	C8—C7—C6	118.7 (6)
C13—C12—C11	115.8 (5)	C8—C7—H7	120.6
C13—C12—H12	122.1	C6—C7—H7	120.6
C11—C12—H12	122.1	O2—C6—C5	122.2 (5)
C12—C11—C4	112.5 (5)	O2—C6—C7	114.9 (5)
C12—C11—C16	120.7 (5)	C5—C6—C7	122.9 (5)
C4—C11—C16	126.8 (5)	C4—N2—C2	113.1 (5)
N2—C4—C11	122.2 (5)	C4—N2—Cr1	125.9 (4)
N2—C4—H4	118.9	C2—N2—Cr1	120.7 (3)
C11—C4—H4	118.9	C3—N1—C1	118.9 (5)
C1—C2—N2	105.6 (5)	C3—N1—Cr1	124.9 (4)
C1—C2—H2A	110.6	C1—N1—Cr1	116.1 (3)
N2—C2—H2A	110.6	Cr1—O3—Cr1[i]	141.1 (3)
C1—C2—H2B	110.6	C16—O1—Cr1	131.2 (4)
N2—C2—H2B	110.6	C6—O2—Cr1	130.1 (4)
H2A—C2—H2B	108.8		

Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

Fig. 1