Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Benzobicyclooctatriene)tetra-carbonylchromium

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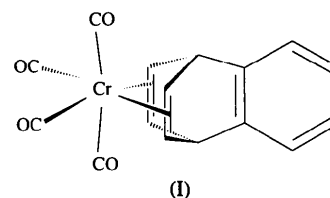Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA

Abstract

(2,3-Benzobicyclo[2.2.2]octa-2,5,7-triene)tetracarbonylchromium, $[Cr(C_{12}H_{10})(CO)_4]$, is a complex of chromium(0) in which the organic ligand is coordinated to the Cr atom through the two free double bonds in a *cis* chelating arrangement. Four terminal carbonyl ligands complete the coordination sphere of the metal. The geometry about the Cr atom is a modestly distorted octahedron formed by the four carbonyl groups and the centroids of the two coordinated double bonds.

Comment

The field of organochromium chemistry has been dominated by the study of (arene)chromium compounds. Of particular interest have been (arene)carbonylchromium compounds which exhibit greater stability with respect to oxidative and thermodynamic decomposition than bis(benzene)chromium. The title compound, (I), was isolated as part of a study of (alkenylarene)chromium compounds. While there exist many examples of (arene)chromium compounds, relatively few complexes with π-bonded alkene ligands are known. Of the (alkene)carbonylchromium complexes that have been reported, most involve alkene moieties that are part of a chelated ligand, such as norbornadiene (Bennett, Pratt & Wilkinson, 1961) and butadiene (von Gustorf, Jaenicke & Polansky, 1972). Theoretical studies have concluded that unconjugated dienes of this type coordinate favourably to the $Cr(CO)_4$ fragment (Elian & Hoffmann, 1975).

(I)

As shown in Fig. 1, the benzobicyclooctatriene ligand bonds to the Cr atom as a chelating diene with the two vertical double bonds occupying *cis* positions in the octahedral coordination sphere. That each alkene moiety is acting as a two-electron π donor is supported by the C5—C6 and C7—C8 distances, which are very close to those of a free double bond. The four carbonyl ligands are bound in almost linear fashion at the remaining vertices of the octahedron. The axial carbonyl groups are bent away from the chelate to give a C14—Cr—C13 angle of 163.4 (3)°, while the two in the equatorial plane are spread slightly apart so that the C15—Cr—C16 angle is 95.4 (3)°. The axial Cr—C bonds are slightly longer than the equatorial Cr—C bonds. The metrical details of the complex (Table 2) are consistent with those
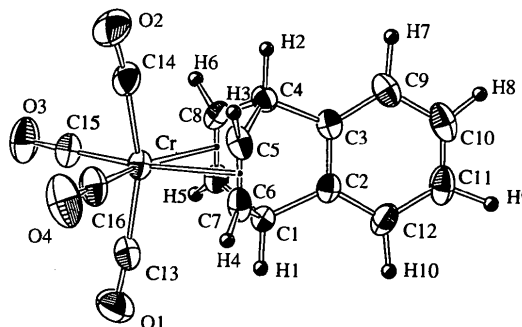

Fig. 1. *ORTEPII* diagram (Johnson, 1976) of the title compound showing the atomic labeling scheme. The displacement ellipsoids of the non-H atoms are shown at the 35% probability level.

reported for the tetracarbonylchromium complexes of hexamethylbicyclohexadiene (Huttner & Mills, 1971), 7,7-dimethoxynorborn-2-ene (Brotherton, Wege, White & Maslen, 1974) and norbornadiene (Jones & Weinkauf, 1991).

Experimental

The 2,3-benzobicyclo[2.2.2]octa-2,5,7-triene ligand was prepared by the reaction of potassium *tert*-butoxide and 2,7-dibromo-5,6-benzobicyclo[2.2.2]oct-5-ene in tetrahydrofuran. The chromium complex was synthesized by the reaction of hexacarbonylchromium (previously refluxed in acetonitrile) and the benzobicyclooctatriene ligand in refluxing glyme. The product was isolated on a silica column with hexane and was recrystallized from a mixture of ether and pentane.

Crystal data

$[Cr(C_{12}H_{10})(CO)_4]$	Mo $K\alpha$ radiation
$M_r = 318.25$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 17
$P2_1/n$	reflections
$a = 11.796\,(8)$ Å	$\theta = 3\text{--}12°$
$b = 7.629\,(4)$ Å	$\mu = 0.799$ mm^{-1}
$c = 15.719\,(5)$ Å	$T = 296$ K
$\beta = 92.65\,(4)°$	Plate
$V = 1413\,(1)$ Å^3	$0.35 \times 0.18 \times 0.05$ mm
$Z = 4$	Yellow–orange
$D_x = 1.496$ Mg m^{-3}	

Data collection

Rigaku AFC-6S diffractom-eter	$\theta_{max} = 25°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 14$
Absorption correction:	$k = 0 \rightarrow 9$
ψ scans (3 reflections)	$l = -19 \rightarrow 19$
$T_{min} = 0.84$, $T_{max} = 1.00$	3 standard reflections
2817 measured reflections	monitored every 150
2681 independent reflections	reflections
1294 observed reflections	intensity decay: <2%
$[I > 3.0\sigma(I)]$	
$R_{int} = 0.072$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.27$ e Å^{-3}
$R = 0.043$	$\Delta\rho_{min} = -0.32$ e Å^{-3}
$wR = 0.039$	Extinction correction: none
$S = 1.71$	Atomic scattering factors
1294 reflections	from Cromer & Waber
190 parameters	(1974), and Cromer
$w = 4F_o^2/\sigma^2(F_o^2)$	(1974)
$(\Delta/\sigma)_{max} = 0.01$	

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cr	0.22239 (7)	0.2126 (1)	0.42350 (6)	3.52 (4)
O1	0.0217 (4)	0.4123 (7)	0.3470 (3)	7.2 (3)
O2	0.3932 (4)	-0.0807 (7)	0.4516 (3)	8.4 (3)
O3	0.0621 (4)	-0.0912 (6)	0.4195 (3)	7.3 (3)
O4	0.2803 (4)	0.1839 (8)	0.2409 (3)	8.7 (3)
C1	0.2058 (4)	0.5345 (7)	0.5222 (3)	3.3 (3)
C2	0.2743 (4)	0.6019 (7)	0.5987 (3)	3.2 (3)
C3	0.3611 (4)	0.4906 (7)	0.6249 (3)	3.4 (3)
C4	0.3657 (4)	0.3248 (7)	0.5717 (3)	3.6 (3)
C5	0.3724 (4)	0.3815 (9)	0.4779 (3)	4.1 (3)
C6	0.2898 (5)	0.4917 (8)	0.4527 (3)	4.0 (3)
C7	0.1637 (4)	0.3530 (7)	0.5435 (3)	3.4 (3)
C8	0.2482 (4)	0.2412 (6)	0.5694 (3)	3.5 (3)
C9	0.4338 (5)	0.5354 (9)	0.6926 (3)	4.6 (3)
C10	0.4185 (5)	0.697 (1)	0.7329 (3)	5.3 (3)
C11	0.3302 (6)	0.8051 (9)	0.7088 (4)	5.3 (3)
C12	0.2571 (5)	0.7581 (7)	0.6412 (4)	4.5 (3)
C13	0.0993 (5)	0.3431 (8)	0.3776 (4)	4.5 (3)
C14	0.3329 (5)	0.0364 (9)	0.4440 (4)	5.2 (4)
C15	0.1229 (5)	0.0257 (8)	0.4201 (4)	4.6 (3)
C16	0.2600 (5)	0.194 (1)	0.3109 (4)	5.4 (3)

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

Cr—C5	2.320 (5)	C14—O2	1.145 (7)
Cr—C6	2.311 (6)	C15—O3	1.144 (6)
Cr—C7	2.303 (5)	C16—O4	1.139 (6)
Cr—C8	2.309 (5)	C1—C6	1.542 (7)
Cr—C13	1.877 (6)	C1—C7	1.514 (7)
Cr—C14	1.890 (7)	C4—C5	1.543 (7)
Cr—C15	1.846 (6)	C4—C8	1.524 (7)
Cr—C16	1.851 (6)	C5—C6	1.333 (7)
C13—O1	1.144 (6)	C7—C8	1.360 (6)
C13—Cr—C14	163.4 (3)	C5—C4—C8	100.5 (4)
C13—Cr—C15	85.4 (3)	C6—C1—C7	101.0 (4)
C13—Cr—C16	83.6 (3)	C4—C5—C6	113.0 (5)
C14—Cr—C15	83.6 (3)	C1—C6—C5	114.1 (5)
C14—Cr—C16	85.2 (3)	C1—C7—C8	113.4 (4)
C15—Cr—C16	95.4 (3)	C4—C8—C7	113.4 (4)
C6—Cr—C7	61.5 (2)	C1—C2—C12	126.4 (5)
C5—Cr—C8	61.2 (2)	C4—C3—C9	126.5 (5)

All H atoms were located on a difference electron density map calculated following anisotropic refinement of the non-H atoms. The H atoms were included in the difference map positions with isotropic displacement parameters equal to 1.2 × B of the attached atom at the time of their inclusion.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983); *DIRDIF* (Beurskens *et al.*, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Dimeric Bis(μ-propionato-O:O')-bis[bis(nicotinamide-N)(propionato-O)zinc(II)]

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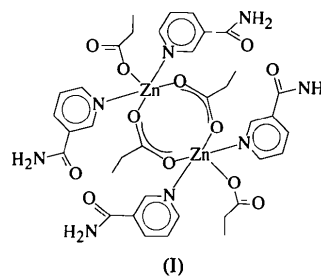
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Abstract

Two bidentate-bridging propionate ligands connect two Zn^{II} atoms [Zn—O(3) 2.040(8) and Zn—O(4)($-x$, $-y$, $-z$) 2.059(4) Å] forming a dimeric

$[Zn_2(C_3H_5O_2)_4(C_6H_6N_2O)_4]$ complex. The coordination around each Zn^{II} atom is trigonal bipyramidal. A monodentate propionate anion completes the trigonal basal plane [Zn—O(1) 2.072(3) Å] and two unidentate nicotinamide ligands occupy the apical positions [Zn—N(11) 2.192(5) and Zn—N(21) 2.174(4) Å] of the coordination sphere of each Zn^{II} atom. The Zn···Zn distance is 3.900(1) Å.

Comment

Complexes where four *syn–syn* carboxylate bridges couple two metal atoms are well known for a wide range of transition metals (Van Niekerk & Schoening, 1953; Mehrotra & Bohra, 1983). In an example of this type of complex containing Zn, $[Zn_2(\text{crotonato})_4(\text{quinoline})_2]$ (Clegg, Little & Straughan, 1986), the metal···metal separation is 2.976(2) Å, but in $[Zn_2(\text{crotonato})_3(\text{crotonato})]$ (Clegg, Little & Straughan, 1986), which has three *syn–syn* bridges, the Zn···Zn distance is longer at 3.247(3) Å. Here we report the structure of $[Zn(C_6H_6N_2O)_2(\mu\text{-}C_3H_5O_2)(C_3H_5O_2)]_2$, (I), which has only two symmetrical *syn–syn* carboxylate bridges and a large Zn···Zn separation of 3.900(1) Å.

(I)

The O atoms of the carboxylate ligands form a triangular equatorial plane around each Zn^{II} atom, the nicotinamide ligands being at apical positions (Fig. 1). The distortion from trigonal bipyramidal geometry around each Zn atom is mainly in the equatorial plane, with one of the angles [O(1)—Zn—O(3)] being about 40° more acute than the other two [O(1)—Zn—O(4^i) and O(3)—Zn—O(4^i); symmetry code: (i) $-x$, $-y$, $-z$]. This can be interpreted as a distortion of the coordination geometry towards a square-pyramidal structure whose stability is comparable with that of the trigonal bipyramid. The ends of the propionate skeleton [C(5)—C(6) and C(2)—C(3)] have large displacements, suggesting the possibility of slight disorder. The short C(5)—C(6) distance of 1.430(23) Å is caused by this disorder.

Hydrogen bonds between the O atom of the carbonyl group and the N atom of the amine group of the nicotinamide ligands link the dimeric molecules into chains in the direction of the *b* axis. These chains are