Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.725$, $T_{max} = 0.801$
5655 measured reflections
5290 independent reflections
4423 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 26.24°$
$h = -11 \rightarrow 0$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections frequency: 120 min intensity variation: negligible

Refinement

Refinement on F
$R = 0.035$
$wR = 0.038$
$S = 1.12$
4423 reflections
442 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.0002$
$\Delta\rho_{max} = 1.37$ e Å^{-3} (0.99 Å from Sm)
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å)*

Sm···Sm^{i}	4.2476 (7)	Sm—O4^{ii}	2.355 (4)
Sm···Sm^{ii}	5.0831 (8)	Sm—O5	2.438 (3)
Sm—O1	2.449 (3)	Sm—O6^{i}	2.358 (4)
Sm—O2^{i}	2.372 (4)	Sm—O7	2.559 (4)
Sm—O3	2.412 (3)	Sm—O8	2.485 (4)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 1-z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O7—H71···O11^{i}	0.854	2.207	2.981 (6)	150.8
O7—H72···O21	0.877	1.882	2.753 (7)	171.8
O8—H81···O9^{ii}	0.986	2.527	3.184 (6)	123.9
O8—H82···O7^{iii}	0.891	1.926	2.787 (5)	162.2
O21—H212···O20^{iv}	0.838	2.435	3.148 (7)	143.5

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, y-1, z$; (iii) $1-x, -y, 1-z$; (iv) $x, y, z-1$.

The water H atoms were found from a difference map. H atoms bonded to C atoms were placed geometrically 0.95 Å from their parent atoms. A riding model was used for all H atoms and their H-atom displacement parameters were fixed as $U_{iso}(H) = 1.3U_{eq}(parent)$.

Data collection and cell refinement: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program used to solve structure: *MolEN*. Program used to refine structure: *MolEN*. Molecular graphics: *MolEN* version of *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*. Other programs include *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1246). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 200–202

Tricarbonyl[(6a,7,8,9,10,10a-η)-3,3-diphenyl-3*H*-benzo[*f*]chromene]chromium

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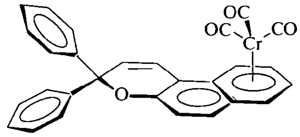
Abstract

The title compound, $[Cr(C_{25}H_{18}O)(CO)_3]$, belongs to a new family of chromenes complexed with tricarbonylchromium and exhibiting photochromic properties. The molecular geometry is compared to that of a similar structure [Hannesschlager *et al.* (1998). *Acta Cryst.* **C54**, 221–223] in which one of the phenyl groups is replaced by a methyl group.

Comment

The photochromic properties of 3*H*-naphthopyrans (2*H*-benzochromenes) (Becker & Michl, 1966) can be modulated by introducing selected substituents onto the different positions of the aromatic system. The complexation of aromatic rings with tricarbonylchromium modifies the reactivity and also the electronic distribution on such structures, which affects the photochromic properties of 3*H*-naphthopyrans. Such behaviour has been observed for indolino spiropyrans (Miyashita *et al.*, 1992) and fulgides (McCabe & Saberi, 1995), and led us to a systematic study of chromenes complexed with tricarbonylchromium. This group improves the photochromic property of the compound by decreasing its fading rate. The red colour is induced by the complexation. We present here the structure of tricarbonyl-[(6a,7,8,9,10,10a-η)-3,3-diphenyl-3*H*-benzo[*f*]chromene]-chromium, (I).



(I)

There are two phenyl groups on the pyran ring at the 2 position, *i.e.* one axial and one equatorial. In the 2-methyl-2-phenyl derivative, the phenyl group is equatorial and the methyl group is axial (Hannesschlager *et al.*, 1998). In this previously reported derivative, the tricarbonylchromium group and the axial methyl group are on the same side of the plane of the chromene system. In the present structure, the tricarbonylchromium and the axial phenyl group are on opposite sides of the plane of the chromene group. Steric interactions probably prevent them from being on the same side in this structure. As in the previous compound, the geometry of the chromene ring is not significantly affected by the presence of the tricarbonylchromium group as compared to the non-complexed derivative (Aldoshin *et al.*, 1996). The conformation of the tricarbonyl group is staggered with respect to the phenyl ring, and the Cr-atom position is not centred on the ring. The average distance of Cr to atoms C8, C9, C10 and C11 is 2.21 (1) Å, while this value is 2.30 (1) Å to atoms C12 and C13. The crystal packing is essentially determined by van der Waals interactions.

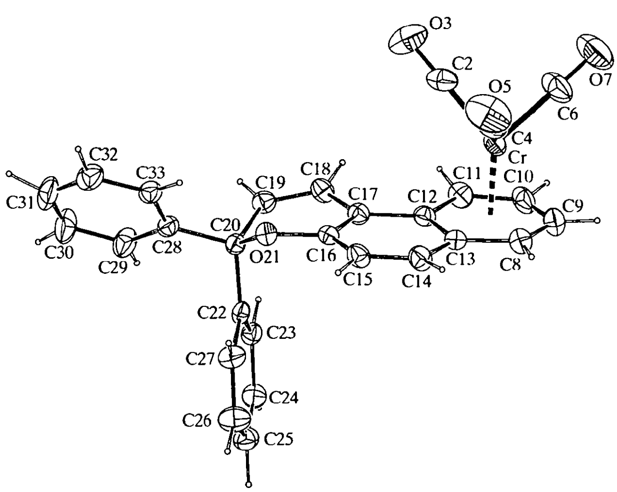


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with displacement ellipsoids plotted at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Experimental

The title compound was prepared from (tripyridine)(tricarbonyl)chromium by an exchange reaction with 3,3-diphenyl-3*H*-naphthopyran (Pozzo *et al.*, 1997; Perez-Encabo *et al.*, 1994). A unique chromium complex was obtained even though there are four aromatic rings available as possible coordination sites. Red needles were obtained by evaporation of a CH_2Cl_2–hexane (1:9) solution.

Crystal data

$[Cr(C_{25}H_{18}O)(CO)_3]$
$M_r = 470.42$
Monoclinic
$P2_1/a$
$a = 8.038$ (2) Å
$b = 20.482$ (4) Å
$c = 13.677$ (3) Å
$\beta = 91.76$ (2)°
$V = 2250.6$ (9) Å^3
$Z = 4$
$D_x = 1.388$ Mg m^{-3}
$D_m = 1.37$ (2) Mg m^{-3}
D_m measured by flotation in benzene/chloroform

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–14°
$\mu = 0.541$ mm^{-1}
$T = 293$ (2) K
Square prism cut from a needle
0.28 × 0.17 × 0.16 mm
Red

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.657$, $T_{max} = 0.917$
6571 measured reflections
6571 independent reflections

4140 reflections with $I > 2\sigma(I)$
$\theta_{max} = 30°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 28$
$l = 0 \rightarrow 19$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.079$
$S = 0.808$
6571 reflections
352 parameters
H atoms refined with $U = 1.2U_{eq}$ of the connected atom, with a length constraint of 1.0±0.05 Å

$w = 1/[\sigma^2(F_o^2) + (0.0009P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.286$ e Å^{-3}
$\Delta\rho_{min} = -0.383$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cr—C4	1.831 (3)	C2—O3	1.173 (3)
Cr—C2	1.815 (3)	C4—O5	1.140 (3)
Cr—C6	1.833 (2)	C6—O7	1.135 (3)
Cr—C11	2.210 (2)	C8—C9	1.413 (3)
Cr—C10	2.204 (2)	C8—C13	1.421 (3)

Cr—C9	2.213 (3)	C9—C10	1.383 (4)
Cr—C8	2.230 (2)	C10—C11	1.380 (3)
Cr—C13	2.299 (2)	C11—C12	1.429 (3)
Cr—C12	2.295 (2)	C12—C13	1.442 (3)
C4—Cr—C2	89.06 (12)	O21—C20—C28	105.83 (13)
C4—Cr—C6	88.24 (13)	C19—C20—C28	110.95 (14)
C2—Cr—C6	87.76 (13)	C22—C20—C28	110.38 (13)
O21—C20—C22	108.08 (12)	C16—O21—C20	115.30 (12)
C19—C20—C22	113.54 (14)		

C14—C15—C16—O21	−179.4 (2)
C12—C17—C18—C19	166.0 (2)
C17—C18—C19—C20	−5.0 (3)
C18—C19—C20—O21	35.6 (2)
C15—C16—O21—C20	−149.49 (15)
C22—C20—C28—C29	−50.6 (2)

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *DATARED* (Pèpe, 1979). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1035). Services for accessing these data are described at the back of the journal.

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