Cl1—As—Cl2	178.60 (2)	Cl2—As—C7	95.73 (6)
Cl1—As—C1	86.00 (6)	Cl2—As—C13	94.86 (6)
Cl1—As—C7	85.52 (6)	C1—As—C7	117.60 (10)
Cl1—As—C13	85.13 (6)	C1—As—C13	123.26 (8)
Cl2—As—C1	92.84 (6)	C7—As—C13	117.35 (10)

Data collection: *STADI4* (Stoe & Cie, 1996*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1394). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 221-223

Tricarbonyl[(4a,5,6,7,8,9-η)-2-methyl-2-phenyl-2*H*-benzo[*f*]chromen]chromium

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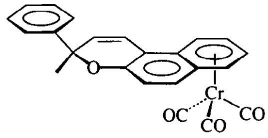
Abstract

The title compound, [Cr($C_{20}H_{16}O$)(CO)$_3$], belongs to a new family of chromene complexes exhibiting photochromic properties.

Comment

3*H*-Naphthopyrans (2-*H*-benzochromenes) exhibit interesting photochromic properties (Becker & Michl, 1966). These properties can be modulated by introducing selected substituents at different positions on the aromatic system. Complexation of the aromatic rings with tricarbonylchromium modifies the reactivity and also the electronic distribution within the structure, and thus we believe that it will modify the photochromic properties of 3*H*-naphthopyrans. Such behaviour has been established in the case of indolino spiropyrans (Miyashita *et al.*, 1992) and fulgides (McCabe & Saberi, 1995). As a result of the presence of three phenyl rings in the title molecule, (I), the crystal structure analysis of this compound has been performed in order to determine the exact tricarbonylchromium position with respect to the rings. The tricarbonylchromium improves the photochromic property of the compound by decreasing its fading rate. The red colour does not indicate an open form, but is induced by the complexation.



(I)

The geometry of the chromene ring is not significantly affected by the presence of the tricarbonylchromium group, if compared with the diphenyl derivative (Aldoshin *et al.*, 1996). However, the bonds of the phenyl ring connected to the Cr atom are longer, the mean value being 1.43 (1) Å instead of 1.40 (1) Å. This is generally the case when phenyl rings are connected to tricarbonylchromium (Schöllkopf *et al.*, 1985).

The conformation of the tricarbonyl group is staggered with respect to the phenyl ring. The Cr-atom position is not centered on the phenyl ring, the average distance to atoms C9, C10 and C11 being 2.20 (1) Å, while it is 2.28 (1) Å to atoms C8, C12 and C13. This displacement is the result of steric interactions between the C22 methyl and the C2=O3 carbonyl groups, as evidenced by the O3···C22 distance of 4.020 (4) Å. The crystal packing occurs essentially through van der Waals interactions.

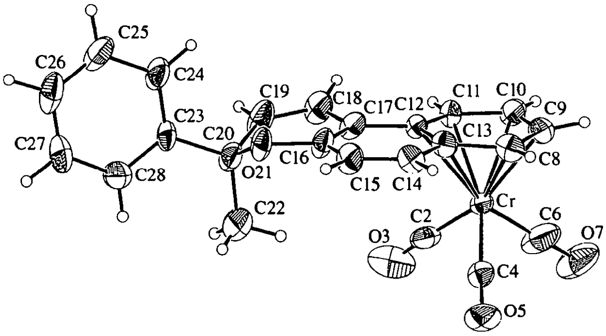


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with displacement ellipsoids plotted at the 50% probability level.

Experimental

The studied compound was prepared starting from (tripyridine)(tricarbonyl)chromium by an exchange reaction with 3-methyl-3-phenyl-3*H*-naphthopyran (Pozzo *et al.*, 1997; Pérez-Encabo *et al.*, 1994). A unique chromium complex was obtained although three aromatic rings are present in the studied system. Red crystals shaped as pseudo-hexagonal platelets were obtained by evaporation of a CH_2Cl_2–hexane (10/90) solution.

Crystal data

$[Cr(C_{20}H_{16}O)(CO)_3]$
$M_r = 408.36$
Monoclinic
$P2_1/c$
$a = 13.832 (3)$ Å
$b = 9.055 (2)$ Å
$c = 16.005 (3)$ Å
$\beta = 104.52 (2)°$
$V = 1940.6 (7)$ Å^3
$Z = 4$
$D_x = 1.398$ Mg m^{-3}
$D_m = 1.40 (2)$ Mg m^{-3}
D_m measured by flotation in benzene/chloroform

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 0.615$ mm^{-1}
$T = 293 (2)$ K
Pseudo-hexagonal platelet
0.39 × 0.23 × 0.19 mm
Red

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.663$, $T_{max} = 0.817$
4036 measured reflections
4036 independent reflections

3032 reflections with $I > 2\sigma(I)$
$\theta_{max} = 34.94°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.085$
$S = 0.955$
4036 reflections
301 parameters
H atoms refined with $U = 1.2U_{eq}$ of the connected atom, with a length constraint of 1.0±0.05 Å.

$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.233$ e Å^{-3}
$\Delta\rho_{min} = -0.236$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cr—C2	1.818 (3)	C10—C11	1.420 (3)
Cr—C4	1.823 (2)	C11—C12	1.431 (2)
Cr—C6	1.817 (3)	C12—C13	1.422 (3)
Cr—C9	2.189 (3)	C12—C17	1.447 (3)
Cr—C11	2.195 (2)	C13—C14	1.467 (3)
Cr—C10	2.204 (2)	C14—C15	1.388 (3)
Cr—C8	2.250 (2)	C15—C16	1.368 (3)
Cr—C12	2.300 (2)	C16—C17	1.389 (3)
Cr—C13	2.301 (2)	C16—O21	1.390 (2)
C2—O3	1.156 (4)	C17—C18	1.418 (3)
C4—O5	1.161 (2)	C18—C19	1.351 (4)
C6—O7	1.168 (3)	C19—C20	1.512 (3)
C8—C9	1.428 (3)	C20—O21	1.442 (3)
C8—C13	1.444 (3)	C20—C23	1.537 (3)
C9—C10	1.423 (4)	C20—C22	1.536 (4)
C2—Cr—C4	88.88 (10)	C19—C20—C23	111.4 (2)
C2—Cr—C6	90.8 (2)	O21—C20—C22	108.6 (2)
C4—Cr—C6	87.33 (10)	C19—C20—C22	107.3 (2)
O21—C20—C19	109.7 (2)	C23—C20—C22	114.3 (2)
O21—C20—C23	105.4 (2)		
C14—C15—C16—O21	−179.4 (2)	C18—C19—C20—O21	29.8 (3)
C12—C17—C18—C19	165.2 (2)	C15—C16—O21—C20	−151.8 (2)
C17—C18—C19—C20	−1.4 (4)	C22—C20—C23—C24	−176.3 (3)

The reflection data were complete to $\theta = 23.5°$. At higher angles, the limits set for the reflection indices caused some truncation of the data.

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: LN1031). Services for accessing these data are described at the back of the journal.

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A Topologically Novel Binuclear Silver Complex of Di-2-pyridyl Sulfide

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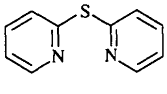
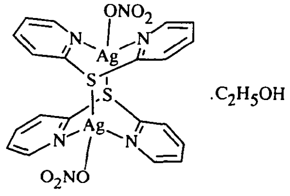
Abstract

The reaction of di-2-pyridyl sulfide with silver nitrate produces a centrosymmetric binuclear complex, bis(di-2-pyridyl sulfide-*N*,*N*′:*S*)bis(nitrato-*O*)-disilver(I) ethanol solvate, $[Ag_2(C_{10}H_8N_2S)_2(NO_3)_2]$.$C_2H_5OH$, within which each Ag atom is coordinated to a monodentate nitrate, an S atom of one ligand and two N atoms of a second ligand. Topologically, this represents the first coordination analogue of the well known photodimers of anthracene.

Comment

During the course of a comprehensive study of the transition metal complexes of chelating heterocyclic ligands, we have investigated the reaction of di-2-pyridyl sulfide, (1), with silver nitrate. Recrystallization of this reaction product from ethanol afforded colourless crystals of a 1:1 metal–ligand stoichiometry, the structure of which we now report. The complex formed is a topologically novel binuclear complex, (2), wherein the ligand displays a mode of coordination not observed previously.


(1)



(2)

The complex crystallizes in the triclinic space group $P\bar{1}$, the asymmetric unit of which comprises an Ag atom chelated to the two N atoms of the ligand and to a monodentate nitrate anion, along with half a molecule of a disordered ethanol solvate. In addition, the Ag atom is coordinated to the S atom of a second ligand, related by a centre of inversion. This results in the assembly of a centrosymmetric binuclear complex (Fig. 1). Although many complexes of (1) have been described (Summers, 1987; Tresoldi *et al.*, 1991), this is the first complex involving coordination of the S atom of the ligand, presumably as a consequence of the thiophilic nature of Ag^I.

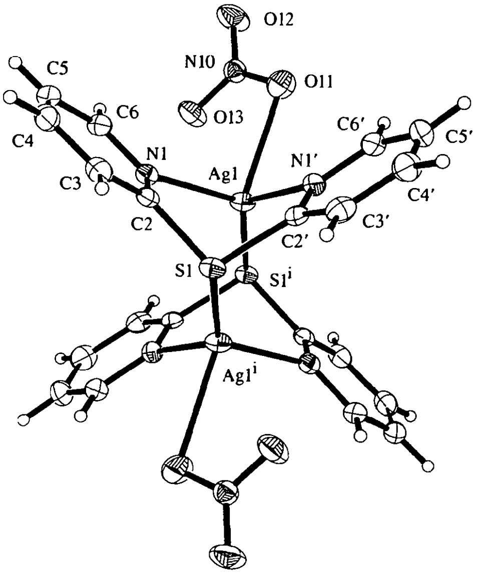


Fig. 1. Perspective view and atom labelling of the binuclear complex (2). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. [Symmetry code: (i) $1 - x, -y, 2 - y$.]

The six-membered chelate ring exists in a boat conformation, wherein the Ag and S atoms lie 1.057 (1) and 0.974 (1) Å, respectively, above the plane defined by N1, C2, N1′ and C2′. A search of the Cambridge Structural Database (Allen & Kennard, 1993) retrieved five X-ray structures of complexes of (1) in which the ligand is chelated through the two N atoms: three Pd^{II} complexes (Tresoldi *et al.*, 1992; De Munno *et al.*, 1993; Nicolo *et al.*, 1996), one V^{IV} complex (Kondo *et al.*, 1995) and one Ru^{II} complex (Bruno *et al.*, 1995). In the