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Chloro(propionyl-*C*)[2(1*H*)-pyridonato-*N*,*O*]bis[tris(1-methylethyl)phosphine]-iridium(III)

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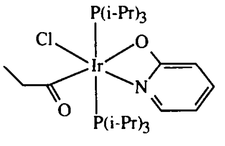
Abstract

The title compound, $[\mathrm{IrCl(C_3H_5O)(C_5H_4NO)\{(C_3H_7)_3P\}_2}]$, is a mononuclear complex of a chelated 2(1*H*)-pyridone anion, exhibiting slightly distorted octahedral geometry. The monohapto carbon-bound propionyl ligand and the O atom of the dihapto pyridonato ligand are mutually *trans*, and the phosphine ligands tilt away from the propionyl ligand towards the O atom of the heterocyclic ligand. The Ir—O bond length is unusually long for a complex of 2(1*H*)-pyridone, a circumstance attributed to the strong *trans* influence of the acyl ligand.

Comment

Recently, we explored the interaction of chloroiridium(I) complexes, tris(1-methylethyl)phosphine and carboxylic acid esters of 2-hydroxypyridine (Grotjahn & Lo, 1995). A product from the reaction of 2-pyridyl propionate is the title $\mathrm{Ir^{III}}$ complex, (I). From spectroscopic data and combustion analysis it was obvious that the diamagnetic complex contained all atoms of the starting ester, two $\mathrm{P(^{\mathit{i}}Pr)_3}$ ligands and a ClIr unit. In particular, four resonances in the ^{1}H NMR spectrum of (I) in the range δ 5.87–9.05 p.p.m. pointed to the pyridonato ligand, and the propionyl ligand was evidenced by a triplet and quartet characteristic of an ethyl group, and by a ^{13}C triplet at δ 196.03 p.p.m., consistent with coupling of the carbonyl C atom to two equivalent ^{31}P nuclei bound to the metal in a mutually *trans* arrangement. The IR spectrum of (I) showed three strong bands at 1617, 1599 and 1489 cm^{-1}, which could be due to an acyl group as well as the heterocyclic ligand.



(I)

The relative disposition of the four non-phosphine ligands in (I) could not, however, be determined by NOE experiments. Furthermore, from the spectral data the hapticity of both the pyridonato and propionyl ligands could not be unambiguously determined; alternative structures for (I) satisfying the 18-electron rule would have either a monohapto acyl and a dihapto heterocyclic ligand, or a dihapto acyl and a monohapto heterocycle. Acyl ligands are most commonly coordinated through carbon only (Redhouse, 1982). However, *C*,*O*-coordination is occasionally observed with late transition metals (Roper, Taylor, Waters & Wright, 1979) but more commonly with early transition metals (for example, Fachinetti, Fochi & Floriani, 1977; for a more recent compilation, see Curtis, Shiu & Butler, 1986). In mononuclear complexes, 2(1*H*)-pyridonato ligands are usually chelated through N and O atoms (Clegg, Berry & Garner, 1980; Rodman & Mann, 1985; Lahuerta, Latorre, Sanaú, Cotton & Schwotzer, 1988; Morrison, Palmer & Tocher, 1988; Leeaphon, Fanwick & Walton, 1991; Steed & Tocher, 1992; Grotjahn, Lo & Groy, 1996). A structurally uncharacterized complex was reported to contain both *N*,*O*-chelating and monohapto pyridonato ligands (Lahuerta, Latorre, Sanaú, Cotton & Schwotzer, 1988).

The complex (Fig. 1) exhibits slightly distorted geometry, with a mutually *trans* orientation of the two phosphines and of the acyl C and heterocyclic O atoms. The phosphines are tilted slightly away from the acyl ligand toward the heterocycle O atom, as evidenced by angles C(7)—Ir(1)—P(1) and C(7)—Ir(1)—P(2) [93.9 (2) and 94.7 (2)°, respectively] and O(2)—Ir(1)—P(1) and O(2)—Ir(1)—P(2) [86.90 (9) and 85.97 (9)°, respectively]. In comparison, the angles between N(1), Ir(1) and the two P atoms [89.21 (12) and 91.96 (12)°] are closer to those of the ideal octahedron, as are the angles between Cl(1), Ir(1) and the two P atoms [88.30 (5) and 88.47 (5)°].

As for the hapticity of the acyl ligand, Roper's group has suggested that the smaller the difference between metal–oxygen and metal–carbon bond lengths, the greater the dihapto character of the acyl ligand (Roper, Taylor, Waters & Wright, 1979). In (I), the Ir(1)—C(7) and Ir(1)···O(1) distances [1.985 (6) and 2.806 (6) Å, respectively] differ by more than 0.8 Å (see Fig. 2), which is far greater than the value of 0.52 Å

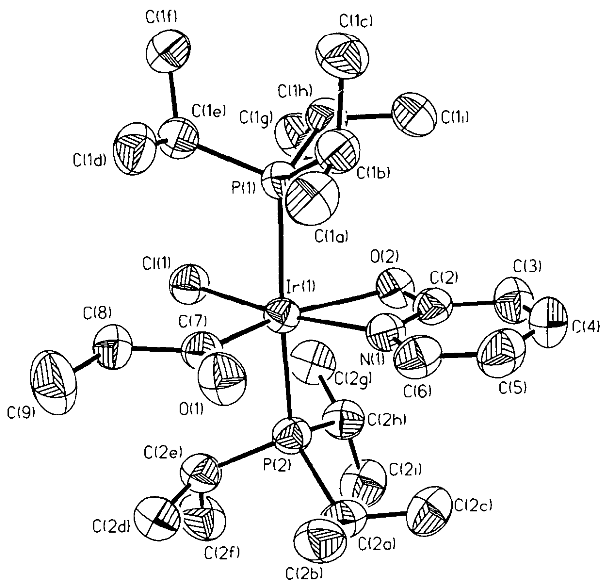


Fig. 1. The title compound shown with displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity.

found by Roper's group for an acyl ligand in an Ru^{II} complex in which the metal–oxygen bond (2.36 Å) was fairly weak. Thus, all the evidence is consistent with coordination of the propionyl ligand through atom C(7) only. A surprising paucity of structurally characterized octahedral Ir^{III} acyl complexes precludes a thorough comparison with data for (I), but the Ir(1)—C(7) and C(7)—O(1) bond lengths are between those of the two molecules found in the literature (Clark, Greene, & Roper, 1985; Milstein, Fultz, & Calabrese, 1986). Moreover, examination of data for Rh^{III} acyls (for example, Lindner, Wang, Mayer, Fawzi & Steimann, 1993; Bianchini, Meli, Peruzzini, Vizza & Bachechi, 1991) shows that in (I), the bond lengths and angles about the acyl carbonyl are unexceptional.

The most prominent distortion of (I) from idealized octahedral geometry is perhaps the N—Ir—O angle of 59.71 (14)°, a consequence of chelation of the heterocycle (see Fig. 2). This angle is within the range of angles reported for chelated pyridonato ligands cited above, but is at the lower end of the range. More unusual, however, is the length of the Ir(1)—O(2) bond [2.344 (3) Å], the value of which is well above the two highest values for metal–oxygen bond lengths in pyridonato-*N*,*O* complexes (each *ca* 2.15 Å: Clegg, Berry & Garner, 1980; Lahuerta, Latorre, Sanaú, Cotton & Schwotzer, 1988) found in our search of the literature. The unusual length of the Ir(1)—O(2) bond is undoubtedly a consequence of the strong *trans* influence of the acyl ligand. An Rh^{III} acyl complex with one ether ligand *trans* to the acyl and another ether ligand *trans* to a phosphine displayed Rh—O bond lengths of 2.385 (6) and 2.236 (5) Å, respectively (Lindner, Wang, Mayer, Fawzi & Steimann, 1993). The strong *trans* influence of a hydride ligand has been used to explain an unusually long metal–nitrogen bond in a pyridonato complex (Grotjahn, Lo & Groy, 1996). The Ir—P bond lengths appear to be unexceptional for Ir[P(^{i}Pr)$_3$]$_2$ complexes (Grotjahn, Lo & Groy, 1996; Grotjahn & Lo, 1995).

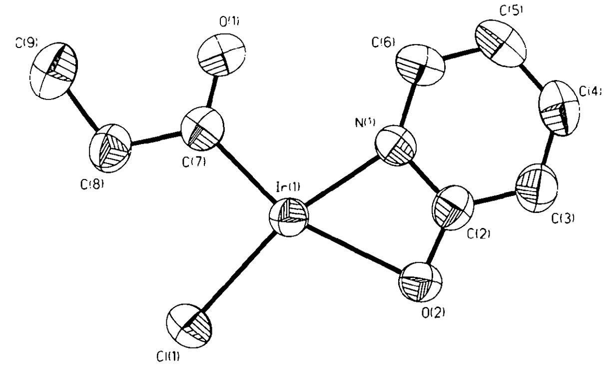


Fig. 2. A view of the title compound as seen normal to the equatorial plane with phosphine ligands omitted.

Experimental

2-Pyridyl propionate, [(cyclooctene)$_2$Ir(μ-Cl)]$_2$ and P(^{i}Pr)$_3$ (molar ratio 1:1:4) were allowed to react in C$_6$D$_6$ at ambient temperature in the dark for 3–5 d. The title complex was isolated by silica gel chromatography under nitrogen as an off-white solid. A crystal was grown from a saturated benzene solution in a nitrogen-filled glovebox by adding about an equal volume of diethyl ether. The flask was capped with a septum and a needle was inserted. Solvent was allowed to evaporate slowly from the resulting assembly in the glovebox at ambient temperature. Colorless rectangular crystals were produced after 3 d. ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 9.05 (*d*, J = 6.0 Hz, 1H), 6.95 (app. *t*, J = 8.3 Hz, 1H), 6.00 (app. *t*, J = 6.8 Hz, 1H), 5.87 (*d*, J = 8.3 Hz, 1H), 3.11 (*q*, J = 6.8 Hz, 2H), 2.53 [*m*, 6H, PC(H)(CH$_3$)CH$_3$], 1.27 [*q*, J = 6.5, 18H, PC(H)(CH$_3$)CH$_3$], 1.25 (*t*, J = 6.8 Hz, 3H), 1.10 p.p.m. [*q*, J = 6.5 Hz, 18H, PC(H)(CH$_3$)CH$_3$]; ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 196.03 (*t*, J = 5.0 Hz), 175.13, 145.52, 138.97, 110.91, 107.45, 44.74, 23.72 (*t*, J = 12.7 Hz), 19.95, 19.82, 10.05 p.p.m.; ^{31}P{^{1}H} NMR (202.3 MHz, C$_6$D$_6$) δ −4.76 p.p.m.; IR (KBr) 1617, 1599, 1489 cm^{-1}; analysis calculated for C$_{26}$H$_{51}$ClIrNO$_2$P$_2$ (699.39) C 44.65, H 7.36, N 2.00%; analysis found C 44.16, H 7.20, N 3.38%.

Crystal data

[IrCl(C$_3$H$_5$O)(C$_5$H$_4$NO)-
(C$_9$H$_{21}$P)$_2$]
M_r = 699.27
Monoclinic
$P2_1/n$
a = 11.782 (3) Å
b = 17.087 (4) Å
c = 14.771 (3) Å
β = 91.29 (2)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25
reflections
θ = 7.5–15°
μ = 4.711 mm^{-1}
T = 293 (2) K
Rectangular parallelepiped
0.40 × 0.20 × 0.20 mm

$V = 2972.9\,(12)$ Å^3
$Z = 4$
$D_x = 1.562$ Mg m^{-3}

Light amber

Data collection

Siemens *P*3 diffractometer
ω scans
Absorption correction:
  ψ scan (*XABS* in *SHELXL*93; Sheldrick, 1993)
  $T_{\min} = 0.135$, $T_{\max} = 0.368$
4417 measured reflections
3914 independent reflections

3447 observed reflections
  $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0276$
$\theta_{\max} = 22.56°$
$h = -12 \rightarrow 12$
$k = -1 \rightarrow 18$
$l = 0 \rightarrow 15$
3 standard reflections
  monitored every 47 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0262$
$wR(F^2) = 0.0688$
$S = 1.023$
3899 reflections
299 parameters
H atoms treated as riding on their parent atoms
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 2.1667P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.008$

$\Delta\rho_{\max} = 0.678$ e Å^{-3}
$\Delta\rho_{\min} = -0.525$ e Å^{-3}
Extinction correction:
  *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient:
  0.00112 (15)
Atomic scattering factors
  from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Ir(1)	0.58859 (2)	0.41530 (1)	0.24091 (1)	0.0414 (1)
Cl(1)	0.58424 (12)	0.52269 (8)	0.13802 (9)	0.0542 (3)
P(1)	0.38884 (12)	0.39951 (8)	0.21312 (9)	0.0459 (3)
P(2)	0.78097 (11)	0.44986 (8)	0.28066 (9)	0.0479 (3)
O(1)	0.6448 (4)	0.2713 (2)	0.1624 (3)	0.0645 (10)
O(2)	0.5421 (3)	0.4654 (2)	0.3831 (2)	0.0496 (8)
N(1)	0.5774 (3)	0.3420 (2)	0.3506 (3)	0.0436 (10)
C(2)	0.5456 (4)	0.3948 (3)	0.4139 (3)	0.0480 (13)
C(3)	0.5193 (5)	0.3696 (4)	0.5016 (4)	0.0595 (15)
C(4)	0.5256 (5)	0.2925 (4)	0.5210 (4)	0.067 (2)
C(5)	0.5606 (5)	0.2388 (4)	0.4564 (4)	0.065 (2)
C(6)	0.5855 (4)	0.2652 (3)	0.3719 (4)	0.0542 (14)
C(7)	0.6311 (4)	0.3403 (3)	0.1448 (4)	0.0494 (13)
C(8)	0.6461 (5)	0.3646 (4)	0.0460 (3)	0.0583 (14)
C(9)	0.6818 (7)	0.2984 (4)	−0.0170 (4)	0.088 (2)
C(1*A*)	0.3804 (5)	0.2319 (3)	0.2238 (4)	0.067 (2)
C(1*B*)	0.3256 (4)	0.3078 (3)	0.2569 (4)	0.0555 (14)
C(1*C*)	0.1976 (5)	0.3014 (4)	0.2452 (4)	0.070 (2)
C(1*D*)	0.3590 (5)	0.3329 (4)	0.0385 (4)	0.064 (2)
C(1*E*)	0.3477 (5)	0.4091 (3)	0.0906 (4)	0.0531 (14)
C(1*F*)	0.2312 (5)	0.4450 (4)	0.0683 (4)	0.068 (2)
C(1*G*)	0.3435 (6)	0.5579 (4)	0.2528 (5)	0.075 (2)
C(1*H*)	0.3006 (5)	0.4754 (4)	0.2690 (4)	0.061 (2)
C(1*I*)	0.2798 (5)	0.4640 (4)	0.3716 (4)	0.074 (2)
C(2*A*)	0.8728 (5)	0.3768 (4)	0.3437 (4)	0.062 (2)
C(2*B*)	0.8718 (6)	0.2953 (4)	0.3028 (5)	0.073 (2)
C(2*C*)	0.8460 (6)	0.3715 (4)	0.4441 (4)	0.072 (2)
C(2*D*)	0.9112 (6)	0.4100 (4)	0.1280 (5)	0.077 (2)
C(2*E*)	0.8645 (5)	0.4792 (4)	0.1811 (4)	0.062 (2)
C(2*F*)	0.9606 (6)	0.5375 (4)	0.1979 (5)	0.082 (2)
C(2*G*)	0.7141 (6)	0.6048 (3)	0.3221 (5)	0.068 (2)
C(2*H*)	0.7787 (5)	0.5340 (3)	0.3601 (4)	0.0585 (14)
C(2*I*)	0.8921 (6)	0.5612 (4)	0.4046 (5)	0.080 (2)

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

Ir(1)—C(7)	1.985 (5)	C(3)—C(4)	1.350 (9)
Ir(1)—N(1)	2.054 (4)	C(4)—C(5)	1.393 (9)
Ir(1)—O(2)	2.344 (3)	C(5)—C(6)	1.365 (8)
Ir(1)—Cl(1)	2.3824 (14)	C(7)—C(8)	1.532 (7)
Ir(1)—P(1)	2.3951 (15)	C(8)—C(9)	1.529 (8)
Ir(1)—P(2)	2.4023 (15)	C(1*A*)—C(1*B*)	1.534 (8)
P(1)—C(1*B*)	1.858 (6)	C(1*B*)—C(1*C*)	1.518 (8)
P(1)—C(1*E*)	1.870 (5)	C(1*D*)—C(1*E*)	1.520 (8)
P(1)—C(1*H*)	1.866 (6)	C(1*E*)—C(1*F*)	1.533 (8)
P(2)—C(2*E*)	1.856 (6)	C(1*G*)—C(1*H*)	1.518 (9)
P(2)—C(2*H*)	1.857 (6)	C(1*H*)—C(1*I*)	1.553 (8)
P(2)—C(2*A*)	1.885 (6)	C(2*A*)—C(2*B*)	1.517 (9)
O(1)—C(7)	1.218 (6)	C(2*A*)—C(2*C*)	1.526 (8)
O(2)—C(2)	1.289 (6)	C(2*D*)—C(2*E*)	1.528 (9)
N(1)—C(2)	1.359 (6)	C(2*E*)—C(2*F*)	1.525 (8)
N(1)—C(6)	1.353 (7)	C(2*G*)—C(2*H*)	1.528 (8)
C(2)—C(3)	1.406 (8)	C(2*H*)—C(2*I*)	1.546 (8)
C(7)—Ir(1)—N(1)	101.1 (2)	C(2*E*)—P(2)—C(2*H*)	107.8 (3)
C(7)—Ir(1)—O(2)	160.8 (2)	C(2*E*)—P(2)—C(2*A*)	105.1 (3)
N(1)—Ir(1)—O(2)	59.71 (14)	C(2*H*)—P(2)—C(2*A*)	102.6 (3)
C(7)—Ir(1)—Cl(1)	92.5 (2)	C(2*E*)—P(2)—Ir(1)	112.8 (2)
N(1)—Ir(1)—Cl(1)	166.37 (12)	C(2*H*)—P(2)—Ir(1)	108.5 (2)
O(2)—Ir(1)—Cl(1)	106.76 (9)	C(2*A*)—P(2)—Ir(1)	119.1 (2)
C(7)—Ir(1)—P(1)	93.9 (2)	C(2)—O(2)—Ir(1)	88.2 (3)
N(1)—Ir(1)—P(1)	89.21 (12)	C(2)—N(1)—C(6)	120.2 (5)
O(2)—Ir(1)—P(1)	86.90 (9)	C(2)—N(1)—Ir(1)	99.3 (3)
Cl(1)—Ir(1)—P(1)	88.30 (5)	C(6)—N(1)—Ir(1)	140.4 (4)
C(7)—Ir(1)—P(2)	94.7 (2)	O(2)—C(2)—N(1)	112.6 (4)
N(1)—Ir(1)—P(2)	91.96 (12)	O(2)—C(2)—C(3)	127.3 (5)
O(2)—Ir(1)—P(2)	85.97 (9)	N(1)—C(2)—C(3)	120.1 (5)
Cl(1)—Ir(1)—P(2)	88.47 (5)	C(4)—C(3)—C(2)	118.8 (6)
P(1)—Ir(1)—P(2)	170.98 (5)	C(3)—C(4)—C(5)	120.9 (6)
C(1*B*)—P(1)—C(1*E*)	108.3 (2)	C(6)—C(5)—C(4)	118.8 (5)
C(1*B*)—P(1)—C(1*H*)	101.6 (3)	N(1)—C(6)—C(5)	121.2 (5)
C(1*E*)—P(1)—C(1*H*)	103.5 (3)	O(1)—C(7)—C(8)	116.6 (5)
C(1*B*)—P(1)—Ir(1)	115.8 (2)	O(1)—C(7)—Ir(1)	120.5 (4)
C(1*E*)—P(1)—Ir(1)	112.8 (2)	C(8)—C(7)—Ir(1)	122.9 (4)
C(1*H*)—P(1)—Ir(1)	113.6 (2)	C(7)—C(8)—C(9)	114.7 (5)

Data were acquired using full 1.50° wide ω scans with a variable scan speed (1.50–14.65° min^{-1}). Background measurements were taken with stationary crystal and detector at the beginning and end of the scan, each for 25% of the total scan time.

Data collection: *P*3/*PC Diffractometer Program* (Siemens, 1989). Cell refinement: *P*3/*PC Diffractometer Program*. Data reduction: *SHELXTL*/*PC* (Sheldrick, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC*. Software used to prepare material for publication: *SHELXTL*/*PC*.

Johnson Matthey Aesar Alfa provided a generous loan of Ir salts.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[*O*-(4-methylcyclohexyl) dithiocarbonato-*S*,*S*′]nickel(II)

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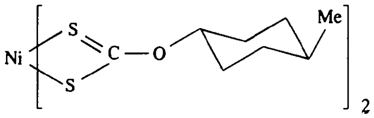
Abstract

The Ni atom in the title compound, [Ni($C_7H_{13}OCS_2$)$_2$], lies on an inversion centre and adopts square-planar coordination geometry defined by the four S atoms of the two dithiocarbonato (xanthate) ligands. The lengths of the two independent Ni—S bonds are equal [2.205 (1) Å].

Comment

Extensive studies have been carried out on the crystal structures, thermal decomposition and spectroscopic properties of alkyl xanthate nickel(II) complexes (Prisyazhnyuk, Bel'skii & Kolchinskii, 1987; Mizota, Fujii & Asahina, 1980; Ballester & Perpinan, 1988). Square-planar xanthate nickel(II) complexes can form adducts using the vacant coordination sites and they readily form clathrates capable of containing a variety of guest molecules (Gable, Hoskins & Winter, 1985; Pang, Lucken & Bernardinelli, 1990). They also have wide technological applications, for example, as oil additives and antioxidants for polyolefins (Klibanov, Dzottsoev & Bushe, 1989; Al-Malaika & Scott, 1983). In an attempt to create a host capable of accepting larger guest molecules, we have prepared the title complex, (I), which is chemically very similar to [Ni($C_2H_5OCS_2$)$_2$] (Prisyazhnyuk *et al.*, 1987), and determined its crystal structure.



(I)

The central Ni atom in (I) is coordinated to a square-planar array of four S atoms. The structure differs from that of [Ni($C_2H_5OCS_2$)$_2$] in which there are two crystallographically independent molecules, with four strong equatorial Ni—S bonds in each molecule and two weak axial bonds to S atoms in other molecules which give each Ni atom distorted octahedral coordination; these octahedra share edges to form a chain structure (Mizota *et al.*, 1980). The four Ni—S bond distances in (I) are equal at 2.205 (1) Å. The Ni—S distances show much greater variation in the five-coordinate complexes Ni($C_2H_5OCS_2$)$_2$.P(C_6H_5)$_3$ [2.225 (2)–2.654 (3) Å] and Ni($C_6H_{11}OCS_2$)$_2$.P(MePh$_2$) [2.210 (2)–2.722 (4) Å], in each of which the Ni atom adopts distorted square-pyramidal coordination geometry, one P and three S atoms describing an approximate basal plane with the apical position being occupied by an S atom from an asymmetrically coordinated xanthate ligand (Tiekink & Winter, 1986; Ballester, Gutierrez-Alonso, Perpinan, Gutierrez-Puebla & Ruiz-Valero, 1990). As expected, almost equivalent S—C bond lengths of 1.692 (3) and 1.696 (3) Å are observed in (I).

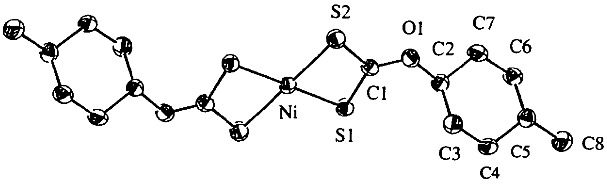


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.