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### ( $\eta^4$ -Cycloocta-1,5-diene)(2-pyridinethiolato *N*-oxide- $\kappa O, \kappa S$ )iridium(I)

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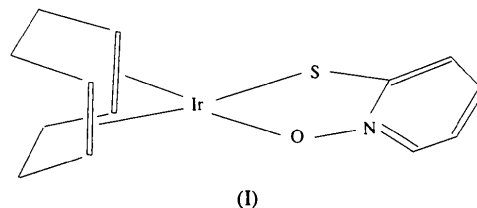
#### Abstract

The title compound, [Ir(C<sub>5</sub>H<sub>4</sub>NOS)(C<sub>8</sub>H<sub>12</sub>)], contains an Ir atom in an approximately square-planar environment if we consider the coordination plane formed by the midpoints of the double bonds of the cyclooctadiene ligand together with the S and O atoms [deviation from least-squares plane is 0.01 (5) Å]. The *S,O*-ligand is also planar and the five-membered chelate ring has a bite angle of 84.4 (3)° at the Ir atom. Bond distances are Ir—S = 2.270 (4), Ir—O = 2.031 (9) and average Ir—C(olefinic) = 2.11 (2) Å.

#### Comment

Iridium complexes are known to serve as homogeneous catalysts in a wide variety of reactions, for example, in the oxidation of various organic compounds, isomerization of alkenes and alkynes, and hydrogenation of multiple C—C bonds (Dickson, 1985). Coordinative unsaturated square-planar Ir<sup>I</sup> complexes are, in general, the best suited for these catalytic reactions owing to their capability to undergo addition reactions. The oxidative addition of specific substrates, for example, H<sub>2</sub>, HI, I<sub>2</sub> and methyl halides, often form an intergal part in these catalytic cycles (Wilkinson, 1987). The isolation and characterization of the title complex, [Ir(C<sub>5</sub>H<sub>4</sub>NOS)(C<sub>8</sub>H<sub>12</sub>)], (I), forms part of our continued research to determine the different factors controlling the rate of oxidative addition (Lewis basicity of complex *via* ligand variation, solvents, addition of halides,

*etc.*) as well as to elucidate the mechanism of oxidative addition between iodomethane and Ir<sup>I</sup> complexes (Theron, Purcell & Basson, 1995).



The olefinic bond lengths of 1.38 (2) Å obtained for the  $\eta^4$ -cycloocta-1,5-diene are normal (Chaloner, Hitchcock & Reisinger, 1992; Abbassioun, Chaloner & Hitchcock, 1990) especially if these are compared with the abnormal metallocyclopropane ring distances in [Ir(C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>S)(C<sub>8</sub>H<sub>12</sub>)] (Theron, Basson & Purcell, 1995) where a structurally similar substituted-thiohydroxamate ligand was used. The Ir—S bond distance in the title complex compares favourably with that of 2.279 (3) Å in the latter structure, which also contains a bidentate ligand with S and O 'bite' atoms. These Ir—S bond distances are, however, significantly longer than those of 2.215 (9) Å in [Ir(sacac)(cod)(CH<sub>3</sub>)I] (sacac = thioacetylacetonato anion; cod = cycloocta-1,5-diene) (Terblans, Basson, Purcell & Lamprecht, 1995) and shorter than those of 2.338 (2) and 2.367 (3) Å in [(cod)Cl(SR)Ir( $\mu$ -SR)<sub>2</sub>Ir(cod)] (*R* = C<sub>6</sub>H<sub>5</sub>) (Fonseca, Hernández, Sanz-Apiricio, Terreros & Torrens, 1994). The decrease in Ir—S bond length for the bidentate ligand which forms a six-membered chelate ring (sacac) is attributed to better orbital overlap compared with the five-membered ring systems. The bite angle of 84.4 (3)° obtained for the bidentate ligand (five-membered ring) in the title complex is significantly smaller than that of *ca* 90° observed for several six-membered chelate rings in Ir and Rh complexes (Botha, Basson & Leipoldt, 1987). The Ir—O bond distance of 2.031 (9) Å in the title complex compares favourably with the corresponding bond distance of 2.05 (2) Å in [Ir(acac)(cod)(CH<sub>3</sub>)I] (acac = acetylacetonato anion) (Basson, Leipoldt, Purcell & Schoeman, 1989).

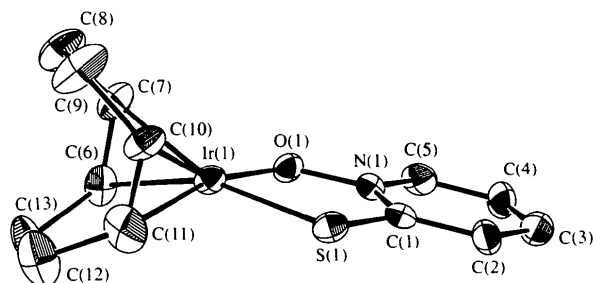


Fig. 1. Perspective view of [Ir(C<sub>5</sub>H<sub>4</sub>NOS)(C<sub>8</sub>H<sub>12</sub>)] indicating the atom labelling. Displacement ellipsoids are drawn at the 25% probability level.

## Experimental

[IrCl(cod)]<sub>2</sub> and 2-pyridinethiolate *N*-oxide (1:2 mol ratio) were mixed in DMF and the addition of water after two minutes precipitated the title compound. Recrystallization was from hot acetone. The density  $D_m$  was measured by flotation in thallium formate.

## Crystal data

[Ir(C<sub>5</sub>H<sub>4</sub>NOS)(C<sub>8</sub>H<sub>12</sub>)] $M_r = 426.53$ 

Monoclinic

 $P2_1/n$  $a = 10.631(2) \text{ \AA}$  $b = 10.840(2) \text{ \AA}$  $c = 11.080(2) \text{ \AA}$  $\beta = 92.31(2)^\circ$  $V = 1275.8(6) \text{ \AA}^3$  $Z = 4$  $D_x = 2.220 \text{ Mg m}^{-3}$  $D_m = 2.2 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 24 reflections

 $\theta = 16\text{--}17^\circ$  $\mu = 10.6 \text{ mm}^{-1}$  $T = 298 \text{ K}$ 

Prismatic

 $0.20 \times 0.20 \times 0.18 \text{ mm}$ 

Yellow

## Data collection

Syntex P1 diffractometer  
 $\theta/2\theta$  scans

Absorption correction:

refined from  $\Delta F$  (Akselrud, Grin, Zavalii, Pecharsky & Fundamunsky, 1989) $T_{\min} = 0.766$ ,  $T_{\max} = 1.000$ 

1589 measured reflections

1589 independent reflections

1531 observed reflections

 $[I > 3\sigma(I)]$  $\theta_{\max} = 27^\circ$  $h = -12 \rightarrow 12$  $k = 0 \rightarrow 12$  $l = 0 \rightarrow 13$ 

3 standard reflections

frequency: 60 min

intensity decay: none

## Refinement

Refinement on  $F^2$  $R = 0.038$  $wR = 0.038$  $S = 0.77$ 

1531 reflections

155 parameters

H atoms calculated, overall

isotropic displacement

parameter refined

Unit weights applied

 $(\Delta/\sigma)_{\max} = 0.097$  $\Delta\rho_{\max} = 1.5 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -1.1 \text{ e \AA}^{-3}$ 

Extinction correction: none

Atomic scattering factors

from Cromer &amp; Mann

(1968)

|       |             |             |             |           |
|-------|-------------|-------------|-------------|-----------|
| C(8)  | 0.5633 (21) | 0.4964 (16) | 0.8424 (14) | 0.074 (5) |
| C(13) | 0.8019 (16) | 0.3579 (18) | 0.7660 (14) | 0.067 (5) |
| C(9)  | 0.5207 (25) | 0.5204 (15) | 0.7153 (15) | 0.090 (7) |
| C(12) | 0.7594 (19) | 0.3929 (22) | 0.6366 (16) | 0.087 (6) |

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| Ir(1)—S(1)        | 2.270 (4)  | Ir(1)—O(1)        | 2.031 (9)  |
| Ir(1)—C(6)        | 2.122 (13) | Ir(1)—C(11)       | 2.07 (2)   |
| Ir(1)—C(10)       | 2.114 (14) | Ir(1)—C(7)        | 2.125 (14) |
| S(1)—C(1)         | 1.717 (14) | O(1)—N(1)         | 1.349 (13) |
| N(1)—C(1)         | 1.37 (2)   | N(1)—C(5)         | 1.36 (2)   |
| C(1)—C(2)         | 1.39 (2)   | C(3)—C(2)         | 1.39 (2)   |
| C(3)—C(4)         | 1.39 (2)   | C(6)—C(7)         | 1.38 (2)   |
| C(6)—C(13)        | 1.55 (2)   | C(5)—C(4)         | 1.36 (2)   |
| C(11)—C(10)       | 1.38 (2)   | C(11)—C(12)       | 1.53 (3)   |
| C(10)—C(9)        | 1.54 (2)   | C(7)—C(8)         | 1.49 (2)   |
| C(8)—C(9)         | 1.48 (2)   | C(13)—C(12)       | 1.53 (2)   |
| S(1)—Ir(1)—O(1)   | 84.4 (3)   | S(1)—Ir(1)—C(6)   | 158.2 (4)  |
| O(1)—Ir(1)—C(6)   | 92.0 (4)   | S(1)—Ir(1)—C(11)  | 94.0 (6)   |
| O(1)—Ir(1)—C(11)  | 163.6 (6)  | C(6)—Ir(1)—C(11)  | 83.4 (7)   |
| S(1)—Ir(1)—C(10)  | 94.5 (4)   | O(1)—Ir(1)—C(10)  | 157.7 (5)  |
| C(6)—Ir(1)—C(10)  | 96.8 (6)   | C(11)—Ir(1)—C(10) | 38.6 (6)   |
| S(1)—Ir(1)—C(7)   | 163.4 (5)  | O(1)—Ir(1)—C(7)   | 92.2 (5)   |
| C(6)—Ir(1)—C(7)   | 37.9 (6)   | C(11)—Ir(1)—C(7)  | 93.8 (7)   |
| C(10)—Ir(1)—C(7)  | 82.6 (6)   | Ir(1)—S(1)—C(1)   | 98.9 (5)   |
| Ir(1)—O(1)—N(1)   | 117.9 (7)  | O(1)—N(1)—C(1)    | 120.2 (10) |
| O(1)—N(1)—C(5)    | 116.9 (11) | C(1)—N(1)—C(5)    | 122.8 (12) |
| S(1)—C(1)—N(1)    | 118.7 (10) | S(1)—C(1)—C(2)    | 123.3 (12) |
| N(1)—C(1)—C(2)    | 118.0 (13) | C(2)—C(3)—C(4)    | 120.1 (14) |
| Ir(1)—C(6)—C(7)   | 71.2 (9)   | Ir(1)—C(6)—C(13)  | 112.8 (9)  |
| C(7)—C(6)—C(13)   | 124 (2)    | N(1)—C(5)—C(4)    | 119.4 (13) |
| Ir(1)—C(11)—C(10) | 72.3 (9)   | Ir(1)—C(11)—C(12) | 113.3 (11) |
| C(10)—C(11)—C(12) | 124 (2)    | Ir(1)—C(10)—C(11) | 69.1 (9)   |
| Ir(1)—C(10)—C(9)  | 110.3 (10) | C(11)—C(10)—C(9)  | 121 (2)    |
| C(1)—C(2)—C(3)    | 119.6 (14) | C(6)—C(7)—C(8)    | 125 (2)    |
| Ir(1)—C(7)—C(8)   | 114.4 (11) | C(7)—C(8)—C(9)    | 113.2 (14) |
| C(3)—C(4)—C(5)    | 120.0 (14) | C(10)—C(9)—C(8)   | 117.9 (14) |
| C(6)—C(13)—C(12)  | 112.1 (13) | Ir(1)—C(7)—C(6)   | 70.9 (8)   |
| C(11)—C(12)—C(13) | 116.0 (14) |                   |            |

*SHELXS86* (Sheldrick, 1985) was used to obtain the position of the heavy atom and *SHELX76* (Sheldrick, 1976) was used (successive Fourier maps) to solve the structure. The H atoms on the  $sp^2$ -hybridized C atoms in the cyclooctadiene group were not located.

Data collection: *XTL/XTLE Structure Determination System* (Syntex, 1976). Cell refinement: *XTL/XTLE Structure Determination System*. Data reduction: *PROFIT* (Streltsov & Zavadnik, 1989). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

|       | $x$         | $y$          | $z$         | $U_{eq}$   |
|-------|-------------|--------------|-------------|------------|
| Ir(1) | 0.54007 (5) | 0.24284 (5)  | 0.72188 (4) | 0.0370 (3) |
| S(1)  | 0.4315 (4)  | 0.1294 (3)   | 0.5805 (3)  | 0.044 (1)  |
| O(1)  | 0.4964 (9)  | 0.1036 (8)   | 0.8354 (8)  | 0.039 (2)  |
| N(1)  | 0.4248 (10) | 0.0103 (10)  | 0.7903 (10) | 0.037 (3)  |
| C(1)  | 0.3867 (13) | 0.0096 (13)  | 0.6705 (13) | 0.042 (3)  |
| C(3)  | 0.2880 (15) | -0.1853 (14) | 0.7057 (14) | 0.058 (4)  |
| C(6)  | 0.6942 (15) | 0.2996 (14)  | 0.8363 (11) | 0.048 (3)  |
| C(5)  | 0.3980 (14) | -0.0824 (13) | 0.8672 (13) | 0.049 (4)  |
| C(11) | 0.6267 (19) | 0.3514 (16)  | 0.5956 (16) | 0.073 (5)  |
| C(10) | 0.5174 (18) | 0.4109 (13)  | 0.6266 (12) | 0.054 (4)  |
| C(2)  | 0.3166 (14) | -0.0903 (14) | 0.6276 (13) | 0.048 (4)  |
| C(7)  | 0.5882 (17) | 0.3632 (14)  | 0.8680 (14) | 0.058 (4)  |
| C(4)  | 0.3301 (15) | -0.1808 (14) | 0.8255 (14) | 0.054 (4)  |

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1135). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Tetrasodium P<sup>1</sup>,P<sup>4</sup>-Bis(5'-adenosyl)-tetraphosphate Dodecahydrate

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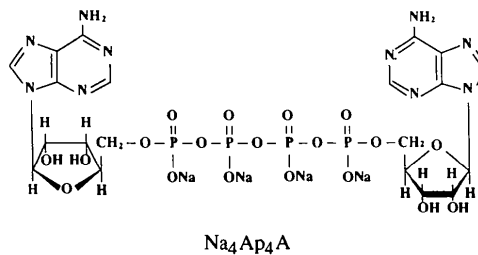
### Abstract

The title compound, 4Na<sup>+</sup>·C<sub>20</sub>H<sub>24</sub>N<sub>10</sub>O<sub>19</sub>P<sub>4</sub><sup>-</sup>·12H<sub>2</sub>O, was found to be the dodecahydrate. The two ribose rings adopt the 3'-endo envelope conformation, with the glycosyl linkage *anti*. The exocyclic side chains have the *g* conformation. The crystal structure is stabilized by interactions involving the Na<sup>+</sup> ions and hydrogen bonds.

### Comment

P<sup>1</sup>,P<sup>4</sup>-Bis(5'-adenosyl)tetraphosphate (Ap<sub>4</sub>A) has various biological activities (Lüthje, 1989). We established the practical enzymatic synthesis of tetrasodium Ap<sub>4</sub>A

(Nakajima, Tomioka, Kitabatake, Dombou & Tomita, 1989) and have developed it for a new medicine. It was very hygroscopic, but we obtained the nonhygroscopic crystal by crystallization with water. Structural analysis showed that it crystallized with 12 water molecules per formula unit.



The two glycosyl torsion angles [O1—C6—N4—C2 -150.1 (4) and O17—C16—N9—C12 -152.1 (4)°] have the *anti* conformation. The two ribose rings adopt the 3'-endo envelope conformation. The pseudorotational phase angles *P* and puckering amplitudes  $\tau_m$  were calculated from the ribose torsion angles (Altona & Sundaralingam, 1972). The values for the C6—C7—C8—C9—O1 ring are *P* = 17.3° and  $\tau_m$  = 37.0°. The values for the C16—C17—C18—C19—O17 ring are *P* = 17.3° and  $\tau_m$  = 38.0°. The exocyclic side-chain torsion angles [O4—C10—C9—C8 47.3 (5) and O14—C20—C19—C18 47.1 (5)°] have the *g* conformation.

Each Na<sup>+</sup> ion is surrounded by six atoms. Na1 is coordinated by two hydroxy O atoms (O2, O3) and four water molecules (O20, O21, O22, O23). Na2 is

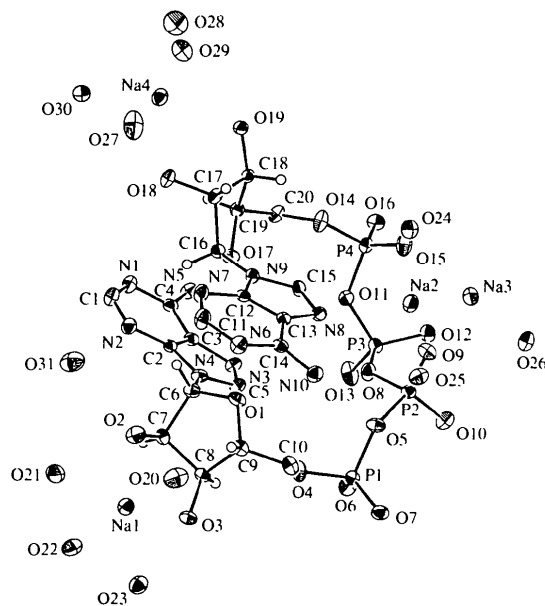


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. Bonds involving Na<sup>+</sup> ions are omitted for clarity.