Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: AB1226). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η⁴-1,5-Cyclooctadiene)(N-hydroxy-4-methoxy-N-methylthiobenzamido-O,S)-iridium(I)

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Abstract

The average olefinic carbon bond length of 1.52 (2) Å in the cyclooctadiene ligand of [Ir(C$_9$H$_{10}$NO$_2$S)(C$_8$H$_{12}$)] is surprisingly long for an olefinic bond (1.34–1.43 Å) and corresponds more closely to an aliphatic carbon bond length (1.54 Å) [Henrici-Olivé & Olivé (1977). *Coordination and Catalysis*, pp. 110–114; *International Tables for X-ray Crystallography*, 1992, Vol. C, Table 9.5.1.1]. The Ir—S and Ir—O bond distances of 2.279 (3) and 2.030 (7) Å, respectively, are normal for this kind of complex [Botha, Basson & Leipoldt (1987). *Inorg. Chim. Acta*, **126**, 25–28].

Comment

Ir^I and Rh^I complexes are used increasingly as catalysts in a number of industrial processes. Examples include the use of [Ir(o-phen)(cod)Cl] (*o*-phen = 1,10-phenanthroline and cod = 1,5-cyclooctadiene) in the conversion of methanol to acetic acid, and the use of [Ir(cod)(PCy$_3$)(py)]PF$_6$ as a catalyst for the hydrogenation of alkenes and alkynes (Dickson, 1985). More often than not, the oxidative addition of a specific substrate, for example H$_2$ or methyl halides, forms an integral part of these catalytic cycles. Four-coordinate complexes, especially square-planar Ir^I and Rh^I complexes, are ideally suited for mechanistic studies of oxidative addition reactions with iodomethane (Basson, Leipoldt, Purcell & Schoeman, 1989; Steyn, Roodt & Leipoldt, 1992). (1,5-Cyclooctadiene)(N-hydroxy-4-methoxy-N-methylthiobenzamido-O,S)iridium(I), the title compound (1), was prepared as a starting material for the high-pressure kinetic study of the oxidative addition reactions between (1) and iodomethane (Theron, Purcell & Basson, 1995).

(1)
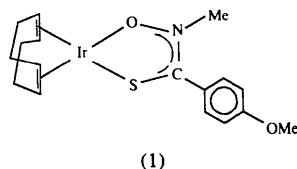
If one considers the coordination plane formed by the centres of the double bonds of the cod ligand and the S and O atoms of the bidentate ligand, Ir has a square-planar environment [with a deviation from the least-squares plane of 0.01 (3) Å]. The olefinic carbon bonds in the cod ligand of the title compound are significantly longer than the corresponding bonds in [Ir(acac)(cod)(CH$_3$)(I)] (Basson, Leipoldt, Purcell & Schoeman, 1989) and [Ir(C≡CC$_6$H$_5$)(η⁴-C$_8$H$_{12}$){P(C$_6$H$_{11}$)$_3$}] (Fernández *et al.*, 1989). The aliphatic carbon bonds C(11)—C(12) and C(15)—C(16) seem short compared to those in other cod structures, but the difference is not significant as there is a relatively large experimental error associated with these bond distances. Similarly, the Ir—C bond *trans* to the S atom is longer than the Ir—C bond *trans* to the O atom, which
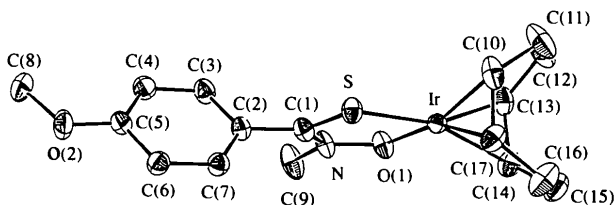

Fig. 1. A perspective view of [Ir(C$_9$H$_{10}$NO$_2$S)(C$_8$H$_{12}$)] with the atom-labelling scheme. The displacement ellipsoids are drawn at the 30% probability level.

is to be expected as a result of the larger *trans* influence of S compared to O (Botha, Basson & Leipoldt, 1987), but the large experimental errors in the bond distances again mean that the difference is not significant.

Experimental

The title complex was crystallized from a saturated acetone solution. The crystal density D_m was measured by flotation in NaI.

Crystal data

$[Ir(C_9H_{10}NO_2S)(C_8H_{12})]$	Mo $K\alpha$ radiation
$M_r = 496.6$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 24
$P2_1/c$	reflections
$a = 12.811$ (3) Å	$\theta = 16-17°$
$b = 10.122$ (1) Å	$\mu = 7.94$ mm^{-1}
$c = 13.176$ (5) Å	$T = 298$ K
$\beta = 95.37$ (3)°	Prismatic
$V = 1701.1$ (8) Å^3	$0.55 \times 0.25 \times 0.20$ mm
$Z = 4$	Yellow
$D_x = 1.94$ Mg m^{-3}	
$D_m = 1.90$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	2793 independent reflections
$\theta/2\theta$ scans	2517 observed reflections
Absorption correction:	$[I > 3\sigma(I)]$
refined from ΔF (Ak-	$R_{int} = 0.0174$
selrud, Grin, Zavalii,	$\theta_{max} = 25°$
Pecharsky & Fun-	$h = -15 \rightarrow 15$
damuntsky, 1989)	$k = 0 \rightarrow 12$
$T_{min} = 0.766$, $T_{max} = 1.000$	$l = -15 \rightarrow 0$
3313 measured reflections	3 standard reflections
	frequency: 60 min
	intensity decay: 1.6%

Refinement

Refinement on F	$\Delta\rho_{max} = 0.9$ e Å^{-3}
$R = 0.032$	$\Delta\rho_{min} = -1.6$ e Å^{-3}
$wR = 0.032$	Extinction correction: none
2517 reflections	Atomic scattering factors
206 parameters	from Cromer & Mann
Unit weights applied	(1968)
$(\Delta/\sigma)_{max} = 0.082$	

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

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

	x	y	z	U_{eq}
Ir	0.67570 (3)	-0.02024 (4)	0.13392 (3)	0.035 (2)
S	0.8073 (2)	0.0268 (3)	0.0349 (2)	0.046 (1)
O(1)	0.6540 (6)	0.1786 (7)	0.1333 (6)	0.048 (2)
N	0.7216 (7)	0.2517 (9)	0.0804 (8)	0.047 (2)
C(1)	0.7945 (8)	0.1963 (11)	0.0325 (9)	0.042 (2)
C(2)	0.8654 (8)	0.2745 (11)	-0.0243 (8)	0.042 (2)
C(3)	0.8297 (9)	0.3497 (11)	-0.1071 (9)	0.050 (3)
C(4)	0.8984 (9)	0.4165 (12)	-0.1638 (9)	0.051 (3)
C(5)	1.0039 (9)	0.4093 (11)	-0.1369 (9)	0.047 (3)
C(6)	1.0429 (9)	0.3346 (11)	-0.0496 (9)	0.046 (3)
C(7)	0.9730 (8)	0.2661 (11)	0.0033 (9)	0.045 (3)
O(2)	1.0800 (6)	0.4721 (9)	-0.1849 (7)	0.062 (2)
C(8)	1.0467 (13)	0.5563 (17)	-0.2701 (10)	0.082 (4)
C(9)	0.6983 (11)	0.3925 (11)	0.0894 (13)	0.069 (4)
C(10)	0.6599 (11)	-0.2241 (12)	0.0948 (11)	0.064 (4)
C(11)	0.5473 (11)	-0.2720 (16)	0.0934 (14)	0.091 (5)
C(12)	0.4737 (10)	-0.1776 (14)	0.1229 (13)	0.072 (4)
C(13)	0.5161 (9)	-0.0476 (12)	0.1674 (10)	0.053 (3)
C(14)	0.5886 (9)	-0.0409 (12)	0.2642 (9)	0.051 (3)
C(15)	0.6213 (12)	-0.1575 (15)	0.3307 (10)	0.070 (4)
C(16)	0.7085 (14)	-0.2350 (17)	0.2958 (11)	0.086 (5)
C(17)	0.7372 (11)	-0.2064 (12)	0.1892 (10)	0.056 (3)

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

Ir—S	2.279 (3)	Ir—O(1)	2.030 (7)
Ir—C(10)	2.129 (12)	Ir—C(13)	2.151 (11)
Ir—C(14)	2.145 (11)	Ir—C(17)	2.141 (12)
S—C(1)	1.723 (11)	O(1)—N	1.377 (11)
N—C(1)	1.302 (14)	N—C(9)	1.462 (14)
C(1)—C(2)	1.464 (14)	C(2)—C(3)	1.37 (2)
C(2)—C(7)	1.394 (14)	C(3)—C(4)	1.38 (2)
C(4)—C(5)	1.37 (2)	C(5)—C(6)	1.43 (2)
C(5)—O(2)	1.369 (13)	C(6)—C(7)	1.37 (2)
O(2)—C(8)	1.44 (2)	C(10)—C(11)	1.52 (2)
C(10)—C(17)	1.53 (2)	C(11)—C(12)	1.42 (2)
C(12)—C(13)	1.52 (2)	C(13)—C(14)	1.51 (2)
C(14)—C(15)	1.51 (2)	C(15)—C(16)	1.47 (2)
C(16)—C(17)	1.51 (2)		
S—Ir—O(1)	84.2 (2)	C(6)—C(5)—O(2)	114.1 (10)
O(1)—Ir—C(10)	161.4 (5)	C(2)—C(7)—C(6)	120.9 (10)
O(1)—Ir—C(13)	89.7 (4)	Ir—C(10)—C(11)	112.3 (9)
S—Ir—C(14)	161.5 (3)	C(11)—C(10)—C(17)	126.1 (13)
C(10)—Ir—C(14)	93.1 (5)	C(11)—C(12)—C(13)	117.7 (11)
S—Ir—C(17)	96.3 (4)	Ir—C(13)—C(14)	69.3 (6)
C(10)—Ir—C(17)	41.8 (5)	Ir—C(14)—C(13)	69.7 (6)
C(14)—Ir—C(17)	81.1 (5)	C(13)—C(14)—C(15)	124.9 (11)
Ir—O(1)—N	116.2 (6)	C(15)—C(16)—C(17)	116.6 (12)
O(1)—N—C(9)	109.8 (9)	Ir—C(17)—C(16)	111.7 (9)
S—C(1)—N	119.4 (8)	Ir—C(14)—C(15)	113.9 (8)
N—C(1)—C(2)	121.7 (10)	C(14)—C(15)—C(16)	114.3 (11)
C(1)—C(2)—C(7)	118.7 (10)	Ir—C(17)—C(10)	68.7 (7)
C(2)—C(3)—C(4)	121.2 (11)	C(10)—C(17)—C(16)	122.5 (13)
C(4)—C(5)—C(6)	120.0 (10)		

H atoms were placed in calculated positions and refined with one overall displacement parameter. The H atoms on the sp^2-hybridized C atoms in the cyclooctadiene group were not located.

*SHELXS*86 (Sheldrick, 1985) was used to obtain the position of the heavy atom. *SHELX*76 (Sheldrick, 1976) was used to solve the structure. These programs were also used to refine the structure.

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$[\mathrm{Ir(C_9H_{10}NO_2S)(C_8H_{12})}]$

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Piperazine Metavanadate Trihydrate

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Abstract

The structure of piperazine-1,4-diium piperazin-1-ium metavanadate trihydrate, $(\mathrm{C_4H_{11}N_2})(\mathrm{C_4H_{12}N_2})\mathrm{V_3O_9}\cdot 3\mathrm{H_2O}$, is orthorhombic, space group *Pbca*, and contains infinite $(\mathrm{V_3O_9^{3-}})_n$ chains running along the *b* axis of the unit cell. These chains form layers running parallel to the (100) plane. The protonated piperazine molecules and three molecules of water are located between the $(\mathrm{V_3O_9^{3-}})_n$ chains, forming hydrogen bonds which contribute to the stabilization of the structure.

Comment

The common feature of the structures of the hydrated metavanadates that have been determined so far is the presence of chains formed by the linking of $\mathrm{VO_5}$ polyhedra, as found in $\mathrm{KVO_3 \cdot H_2O}$ (Christ, Clark & Evans, 1954), $\mathrm{Ca(VO_3)_2 \cdot 2H_2O}$ (Kelsey & Barnes, 1960), $\mathrm{Ca(VO_3)_2 \cdot 4H_2O}$ (Ahmed & Barnes, 1963), $\mathrm{Sr(VO_3)_2 \cdot 4H_2O}$ (Sedlacek & Dornberger-Schiff, 1965), $\mathrm{Cd(VO_3)_2 \cdot 4H_2O}$ (Ulická, 1988) and $\mathrm{Co(VO_3)_2 \cdot 4H_2O}$ (Avtamonova, Trunov & Bezrukov, 1990). The structures of $\mathrm{Ba(VO_3)_2 \cdot 2H_2O}$ (Ulická, Pavelčík & Huml, 1987), $\mathrm{Co(VO_3)_2 \cdot 2H_2O}$ (Murashova, Velikodnii, Potapov & Trunov, 1988) and $\mathrm{Cu(VO_3)_2}$.-

$2\mathrm{H_2O}$ (Leblanc & Ferey, 1989) contain tetrahedrally coordinated V atoms. We describe here the structure of piperazine metavanadate trihydrate, (I).

(I)
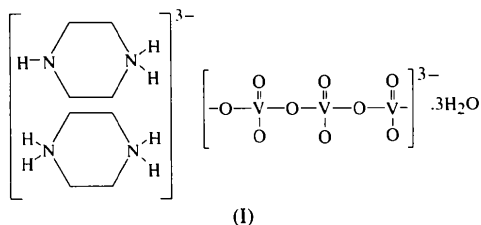
The solution of the structure of piperazine metavanadate trihydrate shows that the asymmetric unit of the crystal structure consists of a $\mathrm{V_3O_9^{3-}}$ unit, which is part of a polymeric anion, two piperazine cations unequally protonated (one cation is doubly protonated and the other is singly protonated) and three molecules of water. The metavanadate anions are infinite chains of $\mathrm{VO_4}$ corner-sharing tetrahedra with each V atom in the centre of a tetrahedron formed by four O atoms. The V—O distances, 1.600 (4)–1.796 (4) Å, are within the range observed in other metavanadate anions. The O—V—O angles are in the range 107.5 (2)–111.5 (2)°, and give no indication of any strong distortion of the tetrahedral environment. The C—N distances in the piperazine cations are within the range observed in the cations in ethylenediammonium vanadate (Bensch, Hug, Reller & Oswald, 1987), *n*-hexylammonium metavanadate (Roman, Aranzabe, Luque & Gutiérrez-Zorrilla, 1991) and 3-aza-1,5-pentamethylenediammonium metavanadate (Roman,
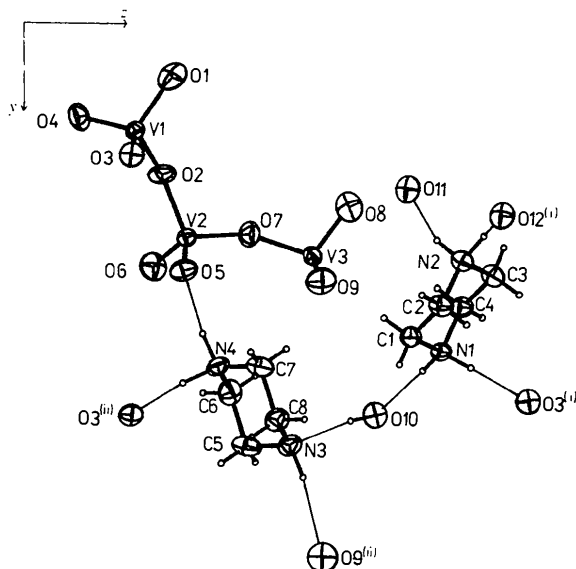
Fig. 1. A fragment of the structure of the title compound showing hydrogen-bonding contacts. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$; (ii) $\frac{1}{2} - x$, $\frac{1}{2} + y$, z.]