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Tetrakis(dimethyl sulfoxide-*O*)copper(II) Bis(perchlorate)

Alexander J. Blake,† Rachel S. Grimditch,† Simon Parsons and Martin Schröder†

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland. E-mail: a.j.blake@nottingham.ac.uk

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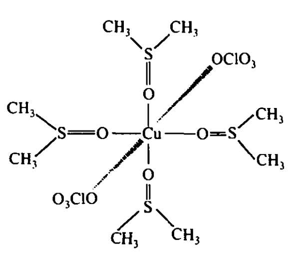
Abstract

The four dimethyl sulfoxide ligands of the title complex, $[Cu(C_2H_6OS)_4]^{2+}.2ClO_4^-$, adopt a tetrahedrally distorted square-planar arrangement around the central Cu^{II} ion, with all Cu—O bond lengths falling within the range 1.934 (6)–1.954 (6) Å. One O atom from each of the axial perchlorate anions interacts weakly at distances of 2.466 (8) and 2.640 (8) Å.

Comment

The dimethyl sulfoxide (DMSO) ligands of the title complex, (I), were found to form a distorted square-planar arrangement around the central Cu^{II} ion, with all angles around the Cu ion close to 90° [O31—Cu—O21 92.1 (3), O11—Cu—O31 86.8 (3), O21—Cu—O41 88.2 (3), O41—Cu—O11 93.5 (3)°]. The Cu ion was found to lie exactly in the mean plane of the four coordinating O atoms; however, there is a tetrahedral distortion at the metal centre, with O11 and O21 lying above [both by 0.105 (3) Å], and O31 and O41 falling below [by 0.106 (4) and 0.104 (3) Å, respectively] this plane. The four S atoms lie on the same side of the O_4 plane, but their deviations from it vary widely: for S1, S2, S3 and S4 these are 0.978 (8), 0.209 (8), 0.582 (9) and 0.092 (9) Å, respectively. There is, in addition, an interaction between the ligands themselves, with each S atom interacting weakly with the O atom of a neighbouring ligand at distances of 2.873 (6)–3.188 (6) Å.



(I)

The C—S bond lengths within the complex [1.754 (10)–1.789 (10) Å] are apparently shorter and the S—O bond lengths [1.505 (6)–1.534 (6) Å] somewhat longer than in uncoordinated sulfoxides [1.81 (3) and 1.497 (13) Å, respectively (Allen *et al.*, 1987)]. Any difference is presumably due to the withdrawal of electron density from the S atom and the diminishing of the S—O double-bond character on coordination.

The structure of (I) differs from the structures of $Cu(DMSO)_2Cl_2$ (Willett & Chang, 1970) and $Cu(DMSO)_2Br_2$ (Willett, Jardine & Roberts, 1977), both of which exhibit five-coordinate geometry around the Cu-atom centre. Both structures contain four normal

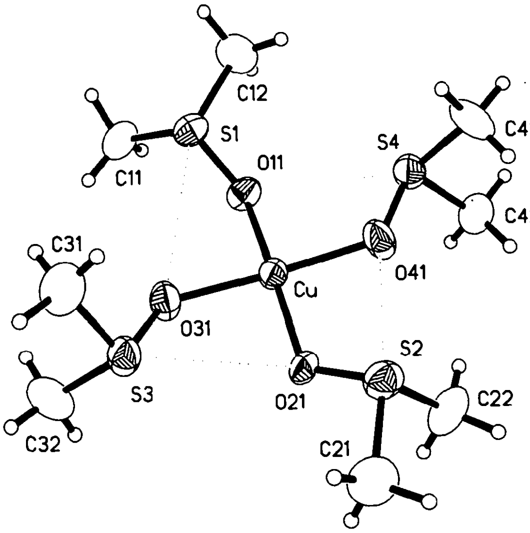


Fig. 1. A view of the complex (I) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. Dotted lines indicate interactions between adjacent coordinated DMSO ligands. The axially coordinated perchlorate anions have been omitted for clarity.

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† Present address: Department of Chemistry, The University of Nottingham, Nottingham NG7 2RD, England.

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Cu–ligand distances and one longer-range interaction with the halide of a neighbouring molecule, with coordination geometry intermediate between square pyramidal and trigonal bipyramidal.

Experimental

The title complex was prepared using the literature method of Selbin, Bull & Holmes (1961) which involves the addition of DMSO (2 ml, 28 mmol) to an ethanolic solution of $Cu(ClO_4)_2.6H_2O$ (2 g, 6 mmol). The complex was recrystallized from acetone and crystals of a quality suitable for X-ray diffraction were grown by diffusion of diethyl ether vapour into a solution of (I) in ethanol.

Crystal data

$[Cu(C_2H_6OS)_4](ClO_4)_2$
$M_r = 574.95$
Monoclinic
$P2_1/a$
$a = 14.280\,(3)$ Å
$b = 10.426\,(2)$ Å
$c = 16.112\,(4)$ Å
$\beta = 112.065\,(14)°$
$V = 2223.1\,(8)$ Å^3
$Z = 4$
$D_x = 1.718$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 52 reflections
$\theta = 10–13°$
$\mu = 1.648$ mm^{-1}
$T = 240.0\,(2)$ K
Column
0.26 × 0.12 × 0.08 mm
Green

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–θ scans with ω scan width $(1.0 + 0.35\tan\theta)°$
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.752$, $T_{\max} = 0.845$
3495 measured reflections

3257 independent reflections
1649 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 25.11°$
$h = -16 \rightarrow 14$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 18$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0649$
$wR(F^2) = 0.1349$
$S = 0.977$
3255 reflections
244 parameters
H atoms placed in calculated positions and thereafter allowed to ride on their parent C atoms with $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$

$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: none
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)

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

	x	y	z	$U_{\rm eq}$
Cu	−0.00265 (9)	0.04887 (12)	0.74794 (8)	0.0333 (3)
S1	−0.2229 (2)	−0.0303 (3)	0.7039 (2)	0.0375 (7)
C11	−0.3174 (7)	0.0891 (10)	0.6802 (7)	0.055 (3)
C12	−0.2628 (8)	−0.1316 (11)	0.7733 (8)	0.068 (4)
O11	−0.1272 (4)	0.0287 (6)	0.7702 (4)	0.037 (2)
S2	0.2180 (2)	0.0079 (3)	0.7684 (2)	0.0452 (8)
C21	0.2998 (8)	0.0796 (12)	0.7200 (8)	0.062 (3)
C22	0.2825 (8)	0.0584 (13)	0.8792 (6)	0.068 (4)
O21	0.1230 (4)	0.0871 (6)	0.7325 (4)	0.040 (2)
S3	−0.0466 (2)	0.1915 (3)	0.5707 (2)	0.0438 (7)
C31	−0.1259 (8)	0.1005 (11)	0.4792 (7)	0.059 (3)
C32	−0.1019 (9)	0.3432 (11)	0.5384 (8)	0.068 (4)
O31	−0.0799 (4)	0.1556 (7)	0.6472 (4)	0.042 (2)
S4	0.0275 (2)	−0.1471 (3)	0.8991 (2)	0.0417 (7)
C41	0.0697 (9)	−0.3060 (10)	0.8981 (7)	0.057 (3)
C42	0.1083 (7)	−0.1002 (10)	1.0097 (6)	0.048 (3)
O41	0.0711 (5)	−0.0733 (7)	0.8395 (4)	0.049 (2)
Cl	0.0864 (2)	0.3082 (3)	0.9173 (2)	0.0400 (7)
O1	0.0216 (7)	0.2207 (9)	0.8590 (6)	0.100 (3)
O2	0.1410 (7)	0.3793 (9)	0.8778 (7)	0.102 (3)
O3	0.0283 (6)	0.3908 (9)	0.9471 (6)	0.093 (3)
O4	0.1548 (8)	0.2422 (11)	0.9899 (7)	0.120 (4)
Cl′	−0.0749 (2)	−0.2663 (3)	0.6153 (2)	0.0412 (7)
O1′	−0.1213 (7)	−0.2962 (8)	0.6754 (6)	0.086 (3)
O2′	−0.0007 (7)	−0.3563 (9)	0.6219 (8)	0.122 (4)
O3′	−0.0306 (7)	−0.1433 (9)	0.6339 (6)	0.093 (3)
O4′	−0.1470 (7)	−0.2646 (12)	0.5291 (6)	0.115 (4)

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

Cu—O41	1.934 (6)	S2—C22	1.754 (10)
Cu—O31	1.936 (6)	S2—C21	1.793 (10)
Cu—O21	1.944 (6)	S3—O31	1.524 (6)
Cu—O11	1.954 (6)	S3—C32	1.757 (11)
S1—O11	1.513 (6)	S3—C31	1.761 (10)
S1—C11	1.770 (10)	S4—O41	1.534 (6)
S1—C12	1.781 (10)	S4—C41	1.765 (11)
S2—O21	1.505 (6)	S4—C42	1.789 (10)
O41—Cu—O31	173.7 (3)	O21—S2—C21	104.1 (4)
O41—Cu—O21	88.2 (3)	C22—S2—C21	98.0 (6)
O31—Cu—O21	92.1 (2)	S2—O21—Cu	125.5 (4)
O41—Cu—O11	93.5 (3)	O31—S3—C32	102.6 (5)
O31—Cu—O11	86.8 (3)	O31—S3—C31	104.3 (5)
O21—Cu—O11	173.7 (3)	C32—S3—C31	99.2 (6)
O11—S1—C11	106.2 (5)	S3—O31—Cu	124.5 (4)
O11—S1—C12	102.4 (5)	O41—S4—C41	104.2 (5)
C11—S1—C12	98.9 (6)	O41—S4—C42	103.0 (4)
S1—O11—Cu	123.8 (3)	C41—S4—C42	99.9 (5)
O21—S2—C22	106.3 (5)	S4—O41—Cu	125.1 (4)

Data collection: *DIF*4 (Stoe & Cie, 1992). Cell refinement: *DIF*4. Data reduction: *X-RED* (Stoe & Cie, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

We thank EPSRC for provision of a four-circle diffractometer and for support (to RSG).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

DOUGLAS B. GROTJAHN, H. C. LO AND THOMAS L. GROY

Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA

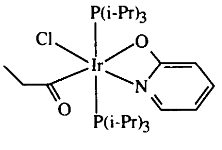
(*Received 22 May 1995; accepted 8 August 1995*)

Abstract

The title compound, $[IrCl(C_3H_5O)(C_5H_4NO)\{(C_3H_7)_3P\}_2]$, 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 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 P(^{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

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