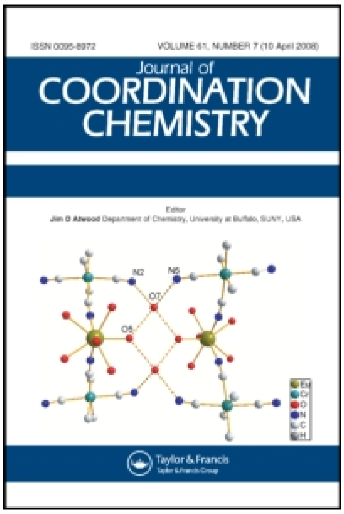

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Synthesis and crystal structure of mercury(II) chloride–ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) adduct

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A mercury(II) chloride adduct of ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid), [$HgCl_2(C_9H_6INO_4)\cdot H_2O$] has been synthesized and characterized by X-ray diffraction analysis and spectroscopic studies. The compound crystallizes in $P2_1/c$ space group, $a = 8.919(3)$, $b = 23.216(3)$, $c = 7.714(3)$ Å, $\beta = 95.79(3)^\circ$. The coordination geometry around mercury is distorted square planar [(2+2) coordination] with two short Hg–Cl bonds [2.308(2) and 2.309(18) Å] and two long Hg–O(sulfonate) [2.738(4) Å] and Hg–O(water) [2.889(4) Å] bonds. The sulfonic group is deprotonated, the proton having migrated to the quinoline N atom that forms intermolecular hydrogen bonds. The inversion related organic ligands are stacked over one another. The crystal structure is further stabilized by a C–H$\cdots$O, O–H$\cdots$O and N–H$\cdots$O hydrogen bonds.

Keywords: Mercury(II) chloride; 7-Iodo-8-hydroxyquinoline-5-sulfonic acid; X-ray diffraction crystal structure analysis; IR spectra; Electronic spectra

1. Introduction

The crystal structures of mercuric chloride [1] and its adducts [2] have been reported. 8-Hydroxyquinoline (oxine) and its derivatives are well known for their antifungal, antibacterial and antiamoebic activities [3]. Chelation of metal cations by 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid (HQS) and their derivatives have long been extensively used in analytical chemistry [4]. Hydrogen bonding patterns and metal-binding modes of sulfoxinates are of current interest. The incorporation of a sulfonic acid group in the oxine molecule offers additional metal binding and hydrogen bonding sites. Previously, the crystal structures of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (ferron) [5], lithium [6], sodium [7], potassium [8], and nickel [9] complexes

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Table 1. Crystallographic data of mercury(II) chloride–ferron adduct.

Empirical formula	$C_9H_6INO_4HgCl_2$
Formula weight	640.62
Temperature (K)	293
Wavelength (nm)	0.071069
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.919(3)
b (Å)	23.216(3)
c (Å)	7.714(3)
α (°)	90
β (°)	95.79(3)
γ (°)	90
V (Å^3)	1477.9(7)
Z	4
Calculated density (g cm^{-3})	2.88
Linear absorption coefficient (mm^{-1})	13.021
$F(000)$	1168.0
Crystal size (mm^3)	$0.29 \times 0.26 \times 0.17$
θ range for data collection (°)	1.8, 28.1
Reflections collected	11486
Independent reflections	3255
Refinement method	Full-matrix least-squares on F^2
Goodness-of- fit on F^2	0.900
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0296$, $wR_2 = 0.0721$
R indices	$R_1 = 0.0355$, $wR_2 = 0.0750$
Largest diff. peak and hole (e Å^{-3})	0.97 & 1.09

of HQS, and magnesium [10], calcium [11], strontium [12], barium [13], cobalt [14], nickel [15], copper [16], zinc [17] and cadmium [18] complexes of ferron have been reported. Thus the crystal structure of the title $HgCl_2$–ferron adduct (**1**) is now presented.

2. Experimental

2.1. *Materials and physical measurements*

Mercuric chloride was purchased from Glaxo and ferron from Riedel de Haen. IR spectrum of the crystal was recorded in KBr pellets with a Perkin–Elmer Spectrum One FT-IR spectrophotometer in the range 4000–400 cm^{-1} and the electronic spectra of the crystal was recorded in H_2O with a Cary 300 Bio UV-visible Varian spectrophotometer in the range of 800–200 nm.

2.2. *Synthesis of mercury chloride ferron*

Hot aqueous solution of ferron (88 mg) and a hot methanolic solution of mercuric chloride (68 mg) were mixed in a 1 : 1 molar ratio. The resultant solution was warmed in a water bath for an hour and then kept at room temperature in order for crystallization to occur. Light yellow crystals were obtained after a few days. IR (cm^{-1}): 3520, 1614, 1542, 1383, 1295, 1207, 1181, 1148, 1089, 1056, 960, 838, 784, 719, 650, 608.

Table 2. Selected bond lengths (Å) and angles (°) for mercury(II) chloride–ferron adduct.

Hg–Cl(1)	2.308(2)
Hg–Cl(2)	2.309(2)
Hg–O(1)	2.738(4)
Hg–O1W	2.889(4)
I1–C7	2.090(5)
S–O1	1.450(4)
S–O2	1.444(5)
S–O3	1.463(4)
S–C5	1.789(5)
O4–C8	1.342(6)
N1–C10	1.372(2)
N1–C2	1.325(3)
Cl(1)–Hg–Cl(2)	174.49(7)
Cl(1)–Hg–O(1)	83.64(11)
Cl(2)–Hg–O(1)	94.20(11)
O1W–Hg–O(1)	152.94(2)
O1–S–O2	115.2(3)
O1–S–O3	112.3(3)
O1–S–C5	104.7(2)
O2–S–O3	111.9(3)
O2–S–C5	105.9(3)
O3–S–C5	105.8(2)
Hg–O1–S	150.1(3)
C2–N1–C10	122.8(5)
N1–C2–C3	120.0(6)
S–C5–C6	118.2(4)
S–C5–C9	121.6(4)
I1–C7–C6	117.7(3)
I1–C7–C8	121.5(4)
O4–C8–C7	128.0(5)
O4–C8–C10	114.5(4)
N1–C10–C9	119.3(5)
N1–C10–C8	118.5(5)

2.3. *Crystal structure determination*

A crystal with dimensions $0.29 \times 0.26 \times 0.17\,\mathrm{mm}^3$ was used for X-ray data collection. All measurements were made on a Bruker AXS diffractometer with graphite monochromated Mo-K_α (0.071073 nm) radiation at 293 K using the ω scan technique. The structure was solved by direct method and refined using SHELXL-97 program [19]. The refinement was carried out by using the full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located through difference Fourier maps. All relevant information about the data collection and the refinement are presented in table 1. Selected bond lengths and angles are given in table 2 and the hydrogen bonding geometry is given in table 3.

3. Results and discussion

The IR spectrum of the complex revealed characteristic changes (as compared with the spectrum of the ligand) confirming complexation. In the electronic spectrum, the intraligand bands are located in the region around 250–285 nm [20]. The band at 399 nm is attributable to the ligand to metal charge transfer. In the crystal structure

Table 3. Hydrogen bonding table of mercury(II) chloride–ferron adduct.

D	H	A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N1	H1	O1W^{i}	0.73(9)	1.96(10)	2.690(7)	175(12)
O4	H10	I1	0.8200	2.8500	3.369(4)	123.00
O4	H10	O3^{ii}	0.8200	2.0300	2.732(5)	143.00
O1W	H11W	O3	0.95(7)	1.96(6)	2.874(6)	160(6)
O1W	H12W	O2	0.95(6)	1.87(5)	2.776(6)	158(5)
C3	H3	Cl1^{iii}	0.89(7)	2.79(7)	3.649(7)	163(5)
C4	H4	O2^{iv}	0.87(7)	2.51(7)	3.183(7)	135(6)
C6	H9	O1	0.93(7)	2.40(6)	2.811(7)	106(5)

Symmetry code: (i) $-x$, $-1/2+y$, $1/2-z$; (ii) x, $1/2-y$, $-1/2+z$; (iii) $1-x$, $-1/2+y$, $1/2-z$; (iv) $1-x$, $-y$, $1-z$.

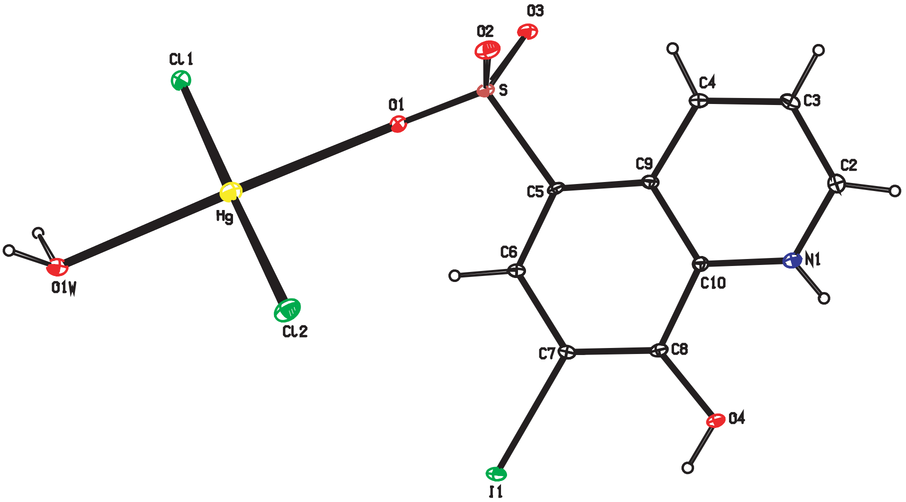

Figure 1. An ORTEP view of the adduct.

of **1**, the asymmetric unit contains $HgCl_2$, 7-iodo-8-hydroxyquinoline-5-sulfonate (ferron) zwitterion and a water molecule. A view of the asymmetric unit is shown in figure 1. In this adduct, the coordination geometry around mercury is distorted square planar with (2+2) coordination. The two collinear covalent Hg–Cl bonds [2.309(18) and 2.308(2) Å] are strong and the two Hg–O bonds [Hg–O(sulfonate) 2.738(4) Å, Hg–O(water) 2.889(4) Å] are relatively longer and weaker. Cl(1)–Hg–Cl(2) bond angle is 174.49(7)° where as the O1W–Hg–O1 bond angle is 152.94(2)°. This type of (2+2) coordination has been reported in many adducts of $HgCl_2$ [21]. There is no Hg–Hg bond in the title compound as the distance between the Hg atoms is 3.674(1) Å, which is longer than the Hg–Hg bonding distance (2.50–2.70 Å) observed in the crystal structure of oxy-mercuric-mercurous chloride [22]. The sulfonic group is deprotonated, the proton having migrated to the quinoline N atom. The protonation of the ring N atom leads to an enhancement in the internal angle at N1 (C10–N1–C2), 122.81°. This value agrees with the crystal structure of ferron [5]. The protonated N atom is hydrogen bonded with a (O1W) water molecule. There is a weak C–H···O intermolecular interaction between C4–H and the O atoms O(2) of the sulfonic group. The hydroxyl group also forms an intermolecular hydrogen bond with one

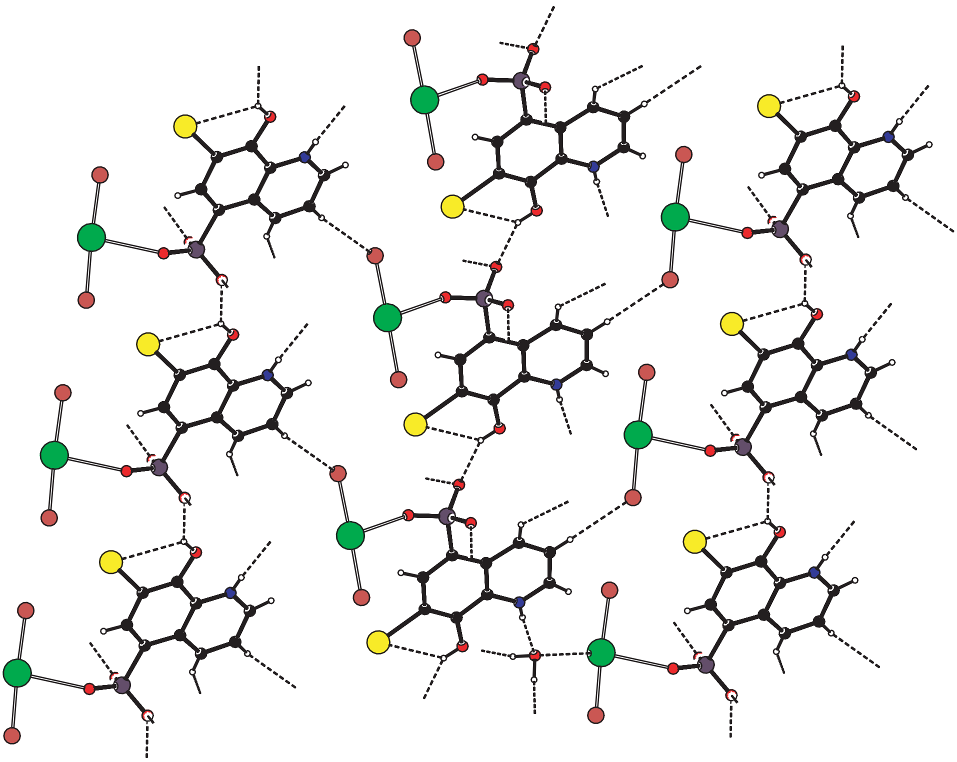

Figure 2. The overall packing arrangement of mercury(II) chloride–ferron adduct.

of the O atoms of the sulfonic group, O(3). Water molecule is hydrogen bonded with O atoms of the sulfonic group, O(3) and O(2) by O–H···O hydrogen bonds. The crystal structure is further stabilized by N–H···O and C–H···Cl hydrogen bonds as shown in figure 2. The intramolecular I···H(10) distance (2.85 Å) is shorter than the van der Waals distance of 3.18 Å, indicating weak bonding interactions between the two atoms. A similar I···H distance of 3.02 Å is observed in cobalt(II) complex of ferron [23]. Regarding π–π stacking, the pyridine and benzene rings are stacked alternatively, with interplanar and centriod-to-centriod distances of 3.572 and 3.8076(4) Å, the corresponding slip angle (the angle between the plane normal and line joining the centriods) being 21.72°.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 249317. Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44 1223 336033.

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