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Synthesis, Spectroscopy and X-ray Studies of [*N'*-(2-Hydroxy-3-Methoxybenzylidene)-4-Methylbenzenesulfonohydrazide]uranyl(IV)[1]

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Abstract—The $C_{30}H_{30}N_4O_{10}S_2U$ complex (**I**) has been investigated and characterized by single crystal X-ray diffraction (CIF file CCDC no. 970349), IR and UV-Vis spectroscopic techniques. X-ray results show that the title compound crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 14.8219(14)$, $b = 11.6177(11)$, $c = 20.0854(15)$ Å, $\beta = 104.268(9)°$, $V = 3351.9(5)$ Å^3 and $Z = 4$. In the title structure, the U atom has a distorted pentagonal-bipyramidal geometry with a tetradentate Schiff base ligand in the equatorial plane and oxo atoms in the axial positions. The C–S–N(H)–N linkage is non-planar, the torsion angle being $-98.7(15)°$ and the S atom showing a tetrahedral environment. The crystal packing occurs intra-inter molecular N–H···O and C–H···O hydrogen bonds.

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INTRODUCTION

Many Schiff base complexes have potential biological interest in an attempt to mimic the structural and functional features of multimetal active sites. Schiff bases have also found useful applications in the synthesis of molecular and supramolecular polymetallic functional systems exhibiting specific optical or magnetic properties [1]. Schiff bases constitute an interesting class of chelating agents, capable of coordination with one or more metal ions to form mononuclear as well as polynuclear metal complexes [2, 3]. Some of their applications can be found in analytical chemistry and serve as biochemical models [4, 5]. Most Schiff bases have antibacterial, anticancer, anti-inflammatory and antitoxic activities [6]; in particular, sulfur-containing Schiff bases are very effective. Schiff bases have played an important role in the devolopment coordination chemistry and Schiff bases ligands are well known their wide range of application in pharmaceutical and industrial field [7, 8]. The coordination compounds derived from Schiff bases with transition metals have been studied with wide scope of their applications [9].

Hydrazones, are used as intermediates in synthesis [10], as functional groups in metal carbonyls [11], in organic compounds [12, 13] and in particular in hydrazone Schiff base ligands [14–17], which are among others employed in dinuclear catalysts [18]. Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelate complexes with transition metals which catalyze physiological processes [19–21]. In analytical chemistry hydrazones find applications as multidentate ligands for transition metals in colorimetric or fluorimetric determinations [22, 23].

In order to acquire more information about uranium(IV) complex, we investigate synthesis, characterization and crystal structure of the $C_{30}H_{30}N_4O_{10}S_2U$ (**I**) mononuclear metal complex by using X–ray diffraction and some spectroscopic techniques. Chemical diagram of compound **I** is the following:

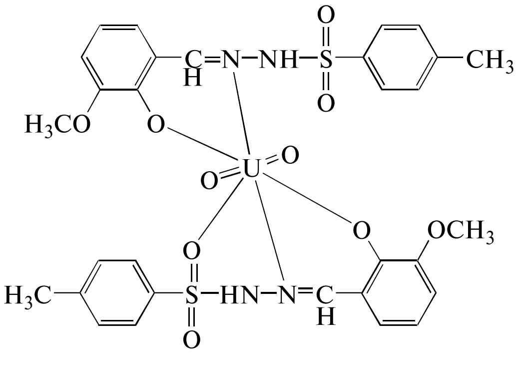

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Table 1. Crystal data and structure refinement parameters of compound **I***

Parameter	Value
Molecular weight	908.73
Temperature, K	296
Wavelength, Å	0.71073
Crystal system	Monoclinic
Crystal size, mm	0.660 × 0.550 × 0.350
Space group	$P2_1/c$
a, Å	14.8219(14)
b, Å	11.6177(11)
c, Å	20.0854(15)
β, deg	104.268(9)
Volume, Å^3	3351.9(5)
Z	4
$T_{\min}$, $T_{\max}$	0.912, 1.000
ρ_{calcd}, mg m^{-3}	1.80
θ Range, deg	3.3–25.0
Index ranges	$-17 \le h \le 17$, $-13 \le k \le 7$, $-22 \le l \le 23$
Measured reflections	12145
Independent reflections	5891
Observed reflections, $I > 2\sigma(I)$	2745
Goodness-of-fit on F^2	1.032
R_1 indice, $I > 2\sigma(I)$	0.091
wR_2 indice, $I > 2\sigma(I)$	0.130

Table 2. Selected bonds (Å) and angles (deg) for **I**

Bond	d, Å	Bond	d, Å
U(1)–O(1)	2.280(12)	N(3)–N(4)	1.448(18)
U(1)–O(4)	2.463(11)	N(1)–C(1)	1.31(2)
U(1)–O(5)	2.212(12)	N(4)–C(9)	1.26(2)
U(1)–O(6)	1.765(10)	S(1)–O(2)	1.416(18)
U(1)–O(7)	1.742(10)	S(1)–O(3)	1.449(16)
U(1)–N(1)	2.556(14)	S(2)–O(4)	1.4716(12)
U(1)–N(4)	2.621(15)	S(2)–O(90	1.430(13)
N(1)–N(2)	1.425(18)		
Angle	ω, deg	Angle	ω, deg
O(1)U(1)O(5)	148.1(4)	O(6)U(1)O(1)	92.5(5)
O(4)U(1)N(1)	150.7(4)	O(6)U(1)N(1)	88.4(5)
O(1)U(1)N(4)	141.1(4)	O(6)U(1)O(5)	88.5(5)
O(1)U(1)O(4)	80.5(4)	N(1)U(1)O(1)	71.4(5)
O(5)U(1)O(7)	92.1(5)	N(1)U(1)O(5)	76.8(5)
O(1)U(1)O(7)	87.6(5)	N(1)U(1)O(7)	92.8(5)
O(4)U(1)O(7)	93.8(5)	N(2)S(1)C(24)	107.9(9)
O(4)U(1)O(5)	131.4(5)	N(3)S(2)C(17)	108.4(10)
O(5)U(1)N(4)	69.5(5)	O(2)S(1)O(3)	122.2(10)
O(4)U(1)N(4)	64.5(4)	O(4)S(2)O(9)	119.1(9)

EXPERIMENTAL

Materials and measurement. The optical absorption spectra of title complex were recorded at room temperature in acetonitrilesolution on a Unicam UV2 UV-VIS spectrometer working between 200 and 900 nm. The infrared (IR) spectra were recorded on a Vertex 80v Bruker FTIR spectrophotometer in 4000–400 cm^{-1} using KBr pellets.

Synthesis of [*N*'-(2-hydroxy-3-methoxybenzylidene)-4-methylbenzenesulfonohydrazide]uranyl(IV) (I). An ethanolic solution (15 mL) of *o*-vanillin (2 mmol, 0.304g) was added to a solution of the 4-methylbenzenesulfonylhydrazine (2 mmol, 0.372 g), in ethanol (15 mL). There sulting solution was stirred for half an hour, and then [$(CH_3COO)_2UO_2 \cdot 2H_2O$] (1 mmol, 0.424 g) in 10 mL ethanol was added. The solution was refluxed for 48 h, with stirring and then allow edto cool at the room temperature. Red crystals of complex were obtained by slowly diffusing, was hed with diethyle the rand finally dried in air for X-ray diffraction analysis (m.p. 249°C and the yield was 74%). IR data (KBr; ν, cm^{-1}): 3187 s ν(N–H), 1592 s ν(C=N), 1453 m ν(C–O), 1260 m ν(C–O_{CH3}), 1327 m, 1164 w, 1108 w, 570 w ν(SO_2), 910 s ν(O=U=O), 543 w ν(U–O),

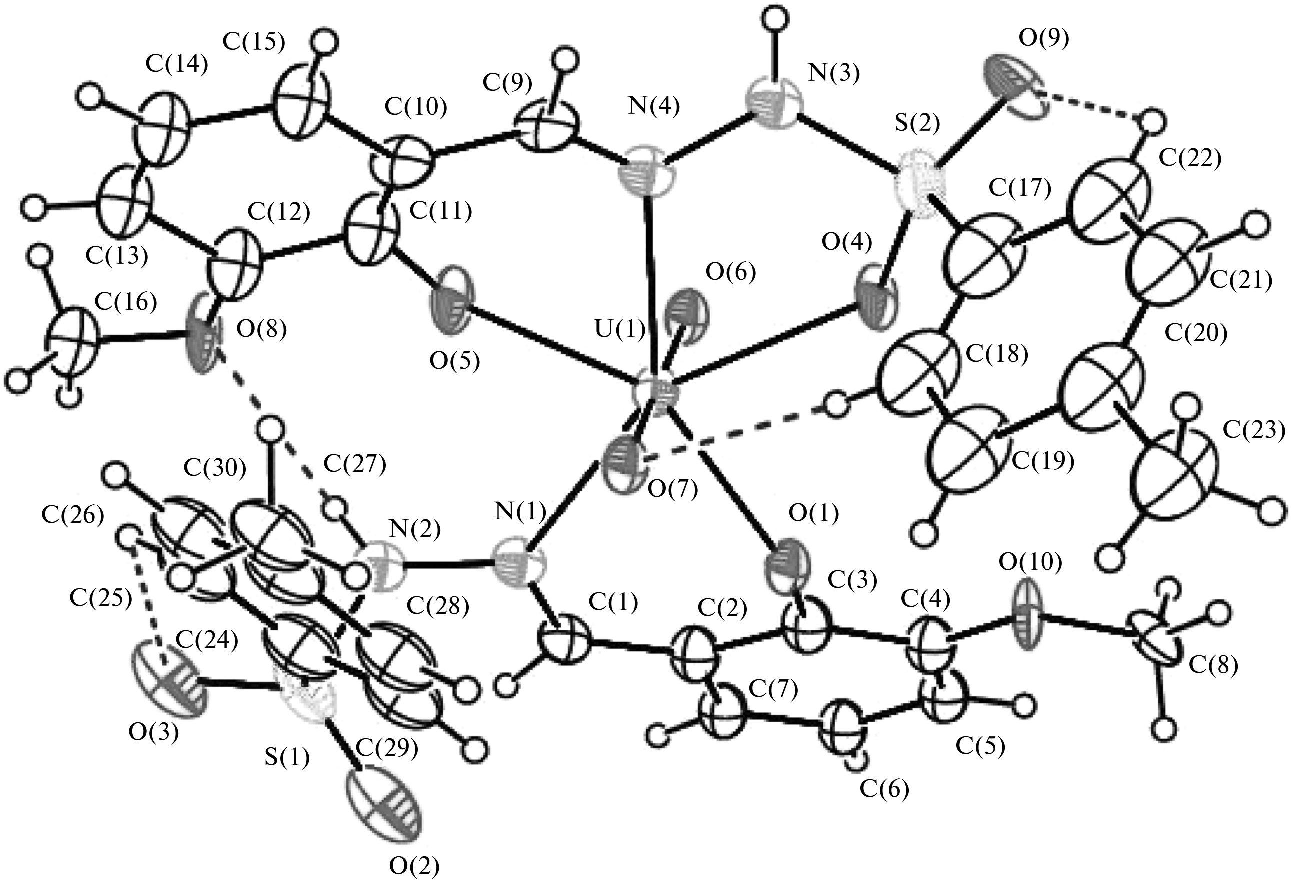

Fig. 1. ORTEP drawing of the molecular structure of **I**, showing the atom numbering scheme and 50% probability displacement ellipsoids with C–H···O and N–H···O intramolecular hydrogen bonding.

451 w ν(U–N), 1510 m ν(C=C), 1469 m, 1370 w ν(C–H), 1180 m, 1072 m, 1032 w, 818 m, 694 w (ν benzene ring bone). UV-Vis data (in chloroform 1.00×10^{-4} M): 279–282 nm ($\pi \to \pi^*$), 327 nm ($n \to \pi^*$), 411 nm (charge transfer transition).

X-ray crystallography. X-ray data collection was carried out an X-AREA diffractometer (Stoe & Cie, 2002); with a graphite monochromatized MoK_α radiation. Cell refinement: X-AREA [24]; data reduction: X-RED32 [24]; program(s) used to solve structure: SHELXS-97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL-97 [25]. Molecular graphics were performed using ORTEP-3 [26]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically. The all hydrogen atoms were included using a riding model and refined isotropically with C–H distances of 0.93–0.97 and N–H 0.86 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ (1.5 for methyl group). Relevant crystal data and details of the structure determinations are given in Table 1.

Supplementary material for **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 970349; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The mononuclear U(IV) atom has a distorted pentagonal-bipyramidal coordination geometry with the Schiff base ligand in the equatorial plane and oxo atoms in the axial positions. The mononuclear metal complex **I** is shown in Fig. 1. The atoms O(1), O(4), and O(5) are displaced by –0.1821(7), 0.2835(8), and 0.1703(8) Å, respectively, from the plane defined by O(1)/N(1)/O(5)/N(4)/O(4). The oxo atoms O(6) and O(7) occupy the axial positions of the metal complex. As can be seen in Table 2, the U(1)–O(6) and U(1)–O(7) bond distances are typical for U=O double bonds, close to those reported previously (1.778(4) and 1.794(5) Å) [27] while the other U–O bond lengths have typical single bond distances. The C–S–N(H)–N sulfonohydrazide linkage is non-planar, the torsion angles being –98.7(15)° and 81.4(15)° for C(17)–S(2)–N3(H)–N(4) and C(24)–S(1)–N2(H)–N(1), respectively, the S atom showing a tet-

Table 3. Geometric parameters of hydrogen bonds for compound **I***

Contect D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(3)–H(3)···O(1)^{i}	0.86	2.25	2.878(17)	130
C(9)–H(9)···O(10)^{i}	0.93	2.43	2.95(2)	115
N(2)–H(2)···O(8)	0.86	2.42	3.01(2)	126
C(18)–H(18)···O(7)	0.94	2.58	3.51(3)	172
C(22)–H(22)···O(9)	0.93	2.54	2.91(3)	104
C(25)–H(25)···O(3)	0.93	2.54	2.89(3)	103

* Symmetry code: ^{i} $1 - x$, $1/2 + y$, $1/2 - z$.

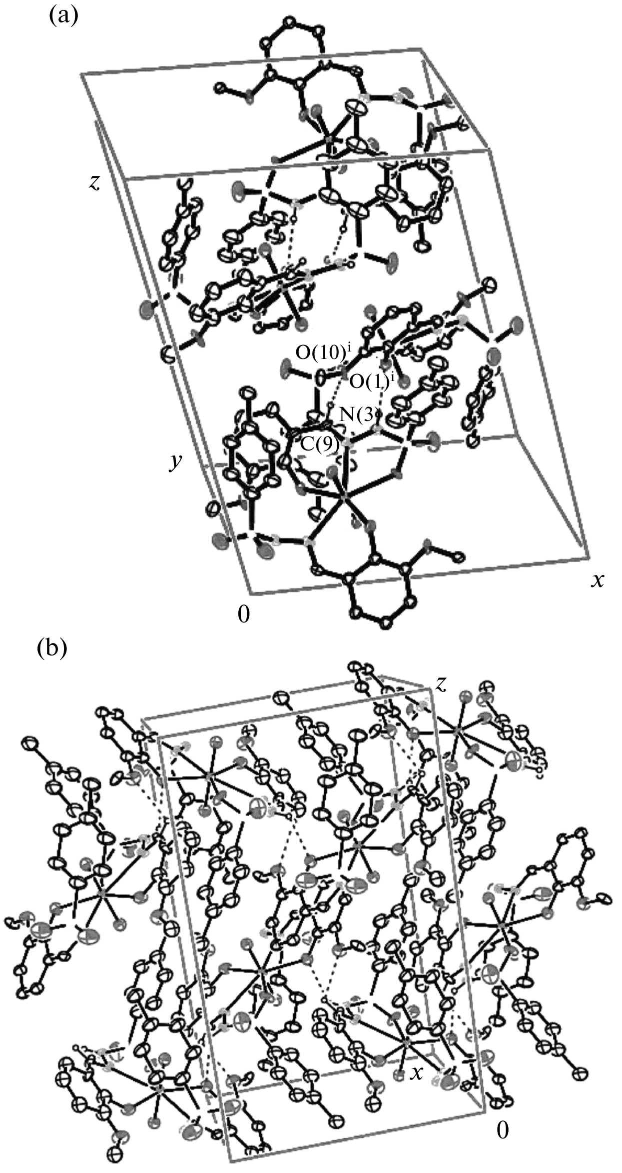

Fig. 2. ORTEP drawing a partial packing diagram of compound **I**. C–H···O and N–H···O interactions have been shown as broken lines. Symmetry code: ^{i} $1 - x$, $1/2 + y$, $1/2 - z$ (a) and drawing an another partial packing diagram (b).

rahedral environment suggests a sp^3 hybridization for the S atom. The dihedral angles between five-six-membered chelate rings, A (UN_2SO), B ($UONC_3$) and C ($UO_5N_4C_3$) are A/B = 10.34(55)°, B/C = 4.36(65)° and A/C = 11.73(58)°.

The crystal packing involves two inter and four intra molecular hydrogen bonds with details of which are given in Table 3. The intra-molecular C–H···O and N–H···O hydrogen bonds are shown in Fig. 1. The inter-molecular C–H···O and N–H···O hydrogen bonds are shown in Fig. 2a and 2b. In these hydrogen bonds, the atoms C(9) and N(3) of molecule at (x, y, z) acts as hydrogen-bond donor, via atoms H(9) and H(3) to the atom O(10) and phenoxide atom O(1) of the molecule at ($1 - x$, $1/2 + y$, $1/2 - z$), respectively centered at (1/2 1/2 1/4) and (1/2 1/2 3/4) and characterized by a $R_2^2(9)$ motif. These hydrogen bonds are shown in Fig. 2a. As can be seen Fig. 2b, $R_2^2(9)$ rings formed by hydrogen bonds lie along [010] and [0–10] (y axis) and stabilize to crystal packing. Beside of these hydrogen bonds, the weak π···π and π···ring interactions also stabilize to crystal packing.

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