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Crystal structure of triethylammonium(5-carboxypyridine-2-thiolato- κ^2 *N,S*)-bis(dimethylsulfoxide- $\kappa^1 S$)-(6-sulfidonicotinato- $\kappa^2 N,S$)ruthenium(II) trihydrate, $C_{22}H_{41}N_3O_9RuS_4$

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Abstract

$C_{22}H_{41}N_3O_9RuS_4$, monoclinic, $P2_1/n$ (no. 14), $a = 8.6882(1)$ Å, $b = 25.5660(1)$ Å, $c = 14.1187(1)$ Å, $\beta = 90.393(1)^\circ$, $V = 3136.01(4)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0220$, $wR_{ref}(F^2) = 0.0561$, $T = 120(1)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of $Ru(DMSO)_4Cl_2$ (0.0484 g, 0.1 mmol) [5], 6-mercaptopyridine-2-thiol (6-H₂mna) (0.0311 g, 0.1 mmol) and trimethylamine (29 µL) in methanol (30 mL) was stirred and refluxed for 6 h. The resultant red solution was concentrated

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.24 × 0.23 × 0.11 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	6.97 mm ⁻¹
Diffractometer, scan mode:	XtaLAB AFC12, ω
θ_{max} , completeness:	2 θ , >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	83126, 6348, 0.027
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 6289
$N(param)_{refined}$:	369
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

to ca. 3 mL under reduced pressure, diethyl ether (10 mL) was added to obtain yellow solids, which were washed with distilled water, diethyl ether and then dried in vacuo. Single crystals of the title complex were obtained by slow evaporation of a solution of acetone at 277 K.

Experimental details

All hydrogen atoms were placed in idealized positions and allowed to ride on their parent atoms. Hydrogen atoms at the oxygen atoms were obtained from a difference Fourier map and fixed for the latter stages of the refinement.

Comment

Transition metal complexes containing nicotinic acid or its derivatives have been extensively studied [6]. The interest derives from: (i) the versatile coordinating modes of nicotinic acids since they have N and O coordination atoms [7–9], (ii) the various supramolecular structures of the complexes association with hydrogen bonds, π - π interaction and metallophilic interaction [10, 11], (iii) the promising biological activities of the complexes, such as antibacterial, antifungal, antitumor, anti-inflammatory and antiviral activity [12–15]. However, we note that Ru complexes with nicotinate ligands are rarely reported. To date, only a limited number of ruthenium complexes containing nicotinic acid and its derivatives have been structurally characterized [14, 16–19]. Herein, we described a structure of a ruthenium complex with 6-mercaptopyridine-2-thiol.

The asymmetric unit of the crystal structure (cf. the figure) is comprised of one cationic $[NET_3H]^+$, one anionic

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Ru1	0.26895(2)	0.45136(2)	0.23212(2)	0.01377(5)
S1	0.20055(5)	0.50674(2)	0.09937(3)	0.01811(9)
S2	0.52526(5)	0.48586(2)	0.27693(3)	0.01812(9)
S3	0.15632(5)	0.49480(2)	0.35010(3)	0.02406(10)
S4	0.05892(5)	0.40171(2)	0.21298(3)	0.01777(9)
O1	0.64311(17)	0.33555(6)	−0.13304(9)	0.0314(3)
O2	0.69688(16)	0.31974(5)	0.01987(9)	0.0265(3)
H2	0.7337	0.2925	−0.0008	0.040*
O3	0.53821(16)	0.25145(5)	0.49809(11)	0.0323(3)
O4	0.29047(15)	0.26892(5)	0.47281(10)	0.0272(3)
O5	−0.01347(17)	0.49983(7)	0.34835(10)	0.0387(4)
O6	0.00914(15)	0.37229(6)	0.29818(9)	0.0290(3)
N1	0.37188(16)	0.42603(5)	0.10516(9)	0.0144(3)
N2	0.39035(16)	0.40107(6)	0.32129(9)	0.0161(3)
C1	0.32227(19)	0.46344(6)	0.04321(12)	0.0161(3)
C2	0.3723(2)	0.46396(7)	−0.05028(12)	0.0188(3)
H2A	0.3384	0.4896	−0.0922	0.023*
C3	0.4731(2)	0.42571(7)	−0.07942(12)	0.0191(3)
H3	0.5073	0.4253	−0.1417	0.023*
C4	0.52417(19)	0.38745(7)	−0.01577(12)	0.0172(3)
C5	0.47127(19)	0.38935(6)	0.07688(11)	0.0157(3)
H5	0.5058	0.3645	0.1202	0.019*
C6	0.6278(2)	0.34487(7)	−0.04857(12)	0.0209(3)
C7	0.52855(19)	0.42562(6)	0.33348(11)	0.0166(3)
C8	0.6458(2)	0.40231(7)	0.38656(12)	0.0201(3)
H8	0.7416	0.4183	0.3927	0.024*
C9	0.6163(2)	0.35486(7)	0.42988(13)	0.0224(4)
H9	0.6928	0.3389	0.4661	0.027*
C10	0.4728(2)	0.33067(7)	0.41980(12)	0.0198(3)
C11	0.3636(2)	0.35496(7)	0.36256(12)	0.0178(3)
H11	0.2691	0.3387	0.3527	0.021*
C12	0.4334(2)	0.27969(7)	0.46713(13)	0.0229(4)
C13	0.2273(3)	0.56024(9)	0.36033(16)	0.0376(5)
H13A	0.3347	0.5594	0.3768	0.056*
H13B	0.1715	0.5784	0.4087	0.056*
H13C	0.2139	0.5781	0.3010	0.056*
C14	0.2086(3)	0.47024(10)	0.46395(14)	0.0356(5)
H14A	0.1721	0.4350	0.4703	0.053*
H14B	0.1632	0.4917	0.5120	0.053*
H14C	0.3186	0.4708	0.4708	0.053*
C15	−0.1098(2)	0.43310(8)	0.16779(14)	0.0269(4)
H15A	−0.1411	0.4602	0.2107	0.040*
H15B	−0.1911	0.4079	0.1613	0.040*
H15C	−0.0881	0.4482	0.1070	0.040*
C16	0.0859(2)	0.35467(8)	0.12179(15)	0.0318(4)
H16A	0.1100	0.3722	0.0636	0.048*
H16B	−0.0068	0.3347	0.1136	0.048*
H16C	0.1690	0.3317	0.1389	0.048*
O7	0.0107(2)	0.32281(10)	0.47440(12)	0.0584(6)
H7A	−0.0035	0.3387	0.4222	0.088*
H7B	0.0880	0.3026	0.4697	0.088*
O8	0.36456(17)	0.22700(7)	0.26790(11)	0.0390(4)
H8A	0.2930	0.2114	0.2974	0.059*
H8B	0.3390	0.2305	0.2100	0.059*
N3	0.65611(19)	0.18888(6)	0.27948(11)	0.0262(3)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H3A	0.5523	0.2038	0.2779	0.031*
C17	0.7514(3)	0.27692(10)	0.23055(17)	0.0472(6)
H17A	0.7935	0.2657	0.1712	0.071*
H17B	0.8074	0.3068	0.2533	0.071*
H17C	0.6451	0.2861	0.2218	0.071*
C18	0.7642(2)	0.23311(8)	0.30183(14)	0.0307(4)
H18A	0.8690	0.2200	0.3027	0.037*
H18B	0.7415	0.2466	0.3644	0.037*
C19	0.6819(3)	0.16475(9)	0.18442(15)	0.0364(5)
H19A	0.6771	0.1921	0.1368	0.044*
H19B	0.5987	0.1404	0.1714	0.044*
C20	0.8330(4)	0.13609(12)	0.17455(19)	0.0541(7)
H20A	0.8444	0.1245	0.1103	0.081*
H20B	0.8343	0.1064	0.2162	0.081*
H20C	0.9162	0.1592	0.1908	0.081*
C21	0.6592(3)	0.15050(8)	0.35977(14)	0.0313(4)
H21A	0.6356	0.1688	0.4180	0.038*
H21B	0.7625	0.1365	0.3660	0.038*
C22	0.5480(3)	0.10573(9)	0.34799(17)	0.0412(5)
H22A	0.5792	0.0843	0.2956	0.062*
H22B	0.4466	0.1192	0.3361	0.062*
H22C	0.5473	0.0851	0.4048	0.062*
O9	0.32388(19)	0.24571(8)	0.08040(11)	0.0425(4)
H9A	0.3866	0.2298	0.0446	0.064*
H9B	0.2345	0.2451	0.0555	0.064*

[Ru(6-mna)(6-Hmna)(DMSO)₂][−] and three water molecules. The ruthenium atom is 6-coordinated by two O atoms from two DMSO ligands and each two N, S atoms from two 6-mercaptopnicotinate anions, namely 5-carboxypyridine-2-thiolate and 6-sulfidonicotinate, which is similar to those of ruthenium complexes with mercaptoppyridine and DMSO ligands [20]. All bond lengths and angles in this title structure are in normal range. Two DMSO ligands adopt monodentate coordination mode, with Ru (1)—S(3) 2.2333(4) Å and Ru (1)—S(4) 2.2377(4) Å. The two sulfido-based ligands adopt bidentate coordination mode, with Ru (1)—N (1) 2.1104(13) Å, Ru (1)—S(1) 2.4197(4) Å, Ru (1)—N (2) 2.0814(14) Å and Ru (1)—S(2) 2.4734(4) Å. The water, carboxylic group and DMSO ligand are both involved in O—H···O hydrogen bonds. In the meantime, the water and trimethylamine are both involved in O—H···N hydrogen bonds.

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