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Crystal structure of 4-phenyl-5-(pyridin-2-yl)-1-((pyridin-2-yl)methyl)-1*H*-imidazole-2(3*H*)-thione, $C_{20}H_{16}N_4S$

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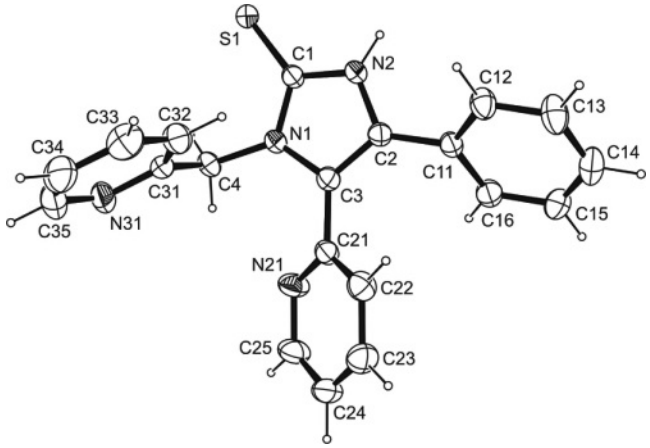

Abstract

$C_{20}H_{16}N_4S$, monoclinic, $P2_1/c$ (no. 14), a = 15.6504(6) Å, b = 5.7055(2) Å, c = 19.4320(7) Å, β = 95.371(2)°, V = 1727.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.0329, $wR_{ref}(F^2)$ = 0.0868, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.22×0.278×0.398 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.97 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23815, 4288
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3734
$N(param)_{refined}$:	230
Programs:	SHELX [8], WinGX [9], MERCURY [10], PLATON [11]

Source of material

The compound was obtained as a by-product upon the attempted coordination of a mixed *ONS* ligand to a rhenium(V) starting material in methanol/dichloromethane. Crystals suitable for the Xray diffraction study were obtained upon free evaporation of the mother liquor at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The nitrogen-bound H atom was located on a difference Fourier map and refined freely.

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Discussion

The synthesis of rhenium-based coordination compounds has been a lively field of research over the past decades [1, 2]. Owing to its potential as being potent radiopharmaceuticals, a vast variety of rhenium coordination compounds featuring many different ligand systems as well as oxidation states have been synthesized and characterized structurally. In continuation of our ongoing research on the field of rhenium(V)-based compounds, the coordination of a mixed *ONS* ligand was attempted upon which an unexpected by-product was obtained. The chemical identity of the latter could be elucidated by means of an Xray diffractometry study on a single crystal that showed it to be a multiply-substituted derivative of a tautomer of imidazole. The title compound contains a thiono-tautomer of imidazole bonded to three aromatic systems, two of them being pyridine or a derivative thereof. The central heterocyclic moiety is essentially flat (r.m.s of all fitted non-hydrogen atoms = 0.0084 Å) with one of the alkene-type carbon atoms deviating most by 0.0127 Å. The small puckering amplitude precludes a conformational analysis [3, 4]. The least-squares plane as defined by the respective non-hydrogen atoms of each aromatic substituent enclose angles of 35.46(4)°, 51.91(4)° and 88.48(4)° with the least-squares plane as defined by the non-hydrogen atoms of the central thiono-tautomer of imidazole. The largest angle is created by the methyl-pyridyl substituent. The angles of intersection among the least-squares planes of the aromatic substituents are measured at 50.11(7)°, 52.21(7)° and 77.68(7)°, respectively. The C=S bond length of 1.6890(12) Å is slightly shorter than the most common values reported for molecular structures featuring comparable N–(C=S)–N moieties in the Cambridge Structural Database [5]. In the crystal, classical N–H···S hydrogen bonds can be observed. The hydrogen bonds connect two molecules to centrosymmetric dimers. In terms of graph-set analysis [6, 7], the descriptor for the N–H···S contacts is $R^2_2(8)$ on the unary level. In addition, C–H···π interactions are apparent exclusively involving hydrogen atoms of pyridine moieties. The shortest intercentroid distance between two centers of gravity was measured at 4.1872(8) Å and rules out any π···π interactions.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(721)	4*e*	0.452(1)	0.650(3)	0.0384(8)	0.038(4)
H(4A)	4*e*	0.1505	0.4319	–0.0431	0.033
H(4B)	4*e*	0.2228	0.3095	–0.0836	0.033
H(12)	4*e*	0.4565	1.1167	0.0720	0.038
H(13)	4*e*	0.5002	1.3648	0.1642	0.049
H(14)	4*e*	0.4393	1.3292	0.2688	0.048
H(15)	4*e*	0.3356	1.0441	0.2817	0.045
H(16)	4*e*	0.2903	0.7981	0.1898	0.039

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(22)	4*e*	0.2093	1.1502	0.0730	0.039
H(23)	4*e*	0.0763	1.2621	0.1094	0.046
H(24)	4*e*	–0.0352	0.9868	0.1065	0.044
H(25)	4*e*	–0.0107	0.6125	0.0669	0.046

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(32)	4*e*	0.2770	0.8641	–0.1091	0.041
H(33)	4*e*	0.2358	1.0891	–0.2081	0.054
H(34)	4*e*	0.1167	0.9702	–0.2818	0.060
H(35)	4*e*	0.0425	0.6397	–0.2545	0.060

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.39744(2)	0.31773(6)	–0.07201(2)	0.0228(1)	0.0433(2)	0.0252(2)	–0.0001(1)	0.0014(1)	–0.0085(1)
N(1)	4*e*	0.26906(6)	0.5547(2)	–0.01597(5)	0.0194(4)	0.0310(5)	0.0244(5)	–0.0035(4)	0.0006(3)	–0.0035(4)
N(2)	4*e*	0.39567(6)	0.6509(2)	0.02880(5)	0.0185(4)	0.0359(5)	0.0229(5)	–0.0025(4)	0.0002(3)	–0.0029(4)
N(21)	4*e*	0.11086(6)	0.6526(2)	0.05022(6)	0.0222(5)	0.0339(6)	0.0489(6)	–0.0034(4)	0.0072(4)	–0.0053(5)
N(31)	4*e*	0.11257(7)	0.5552(2)	–0.16838(6)	0.0302(5)	0.0565(8)	0.0298(6)	–0.0089(5)	–0.0038(4)	–0.0039(5)
C(1)	4*e*	0.35417(7)	0.5110(2)	–0.01933(6)	0.0202(5)	0.0326(6)	0.0212(5)	–0.0025(4)	0.0008(4)	0.0007(4)
C(2)	4*e*	0.33874(7)	0.7808(2)	0.06331(6)	0.0220(5)	0.0309(6)	0.0222(5)	–0.0037(4)	0.0033(4)	–0.0002(4)
C(3)	4*e*	0.25837(7)	0.7245(2)	0.03485(6)	0.0221(5)	0.0283(6)	0.0242(5)	–0.0037(4)	0.0023(4)	–0.0017(4)
C(4)	4*e*	0.20309(7)	0.4615(2)	–0.06630(6)	0.0209(5)	0.0308(6)	0.0293(6)	–0.0058(4)	–0.0010(4)	–0.0041(5)
C(11)	4*e*	0.36802(7)	0.9357(2)	0.12130(6)	0.0226(5)	0.0288(6)	0.0227(5)	–0.0014(4)	–0.0007(4)	–0.0004(4)
C(12)	4*e*	0.43118(8)	1.1028(2)	0.11440(6)	0.0343(6)	0.0362(7)	0.0248(6)	–0.0091(5)	0.0003(5)	0.0024(5)
C(13)	4*e*	0.4574(1)	1.2494(3)	0.16929(7)	0.0486(8)	0.0363(7)	0.0355(7)	–0.0154(6)	–0.0057(6)	–0.0001(6)
C(14)	4*e*	0.4215(1)	1.2281(3)	0.23137(7)	0.0514(8)	0.0368(7)	0.0297(7)	–0.0011(6)	–0.0077(6)	–0.0074(6)
C(15)	4*e*	0.35974(9)	1.0597(3)	0.23884(7)	0.0400(7)	0.0486(8)	0.0237(6)	0.0014(6)	0.0028(5)	–0.0042(6)
C(16)	4*e*	0.33286(8)	0.9137(2)	0.18430(6)	0.0295(6)	0.0417(7)	0.0269(6)	–0.0058(5)	0.0040(5)	–0.0007(5)
C(21)	4*e*	0.17478(7)	0.8104(2)	0.05270(6)	0.0217(5)	0.0304(6)	0.0244(5)	–0.0020(4)	0.0005(4)	0.0004(5)
C(22)	4*e*	0.16375(8)	1.0403(2)	0.07323(7)	0.0318(6)	0.0299(6)	0.0355(7)	–0.0016(5)	0.0014(5)	0.0003(5)
C(23)	4*e*	0.08493(9)	1.1065(3)	0.09406(7)	0.0412(7)	0.0337(7)	0.0401(7)	0.0094(6)	0.0032(6)	–0.0029(6)
C(24)	4*e*	0.01931(8)	0.9455(3)	0.09230(7)	0.0269(6)	0.0484(8)	0.0363(7)	0.0094(6)	0.0050(5)	0.0006(6)
C(25)	4*e*	0.03502(8)	0.7228(3)	0.06934(8)	0.0223(6)	0.0432(8)	0.0508(8)	–0.0028(5)	0.0074(5)	–0.0030(6)
C(31)	4*e*	0.18134(7)	0.6229(2)	–0.12699(6)	0.0218(5)	0.0329(6)	0.0249(5)	0.0005(4)	0.0027(4)	–0.0069(5)
C(32)	4*e*	0.22876(8)	0.8203(2)	–0.13976(7)	0.0331(6)	0.0340(7)	0.0356(7)	–0.0033(5)	0.0018(5)	–0.0031(5)
C(33)	4*e*	0.2045(1)	0.9526(3)	–0.19807(8)	0.0529(8)	0.0398(8)	0.0422(8)	0.0018(7)	0.0101(6)	0.0060(6)
C(34)	4*e*	0.1345(1)	0.8833(3)	–0.24123(8)	0.0543(9)	0.064(1)	0.0317(7)	0.0128(8)	0.0028(6)	0.0093(7)
C(35)	4*e*	0.0910(1)	0.6862(3)	–0.22448(8)	0.0398(7)	0.077(1)	0.0314(7)	–0.0036(8)	–0.0077(6)	0.0009(7)

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