Refinement of the crystal structure of 2-{2-[2-(1*H*-benzo[*d*]imidazol-2-ylphenyl)disulfanyl]phenyl}-1*H*-benzo[*d*]imidazole-*N*,*N'*-diium sulfate tetrahydrate, $[C_{26}H_{20}N_4S_2][SO_4] \cdot 4H_2O$, *at 100 K*

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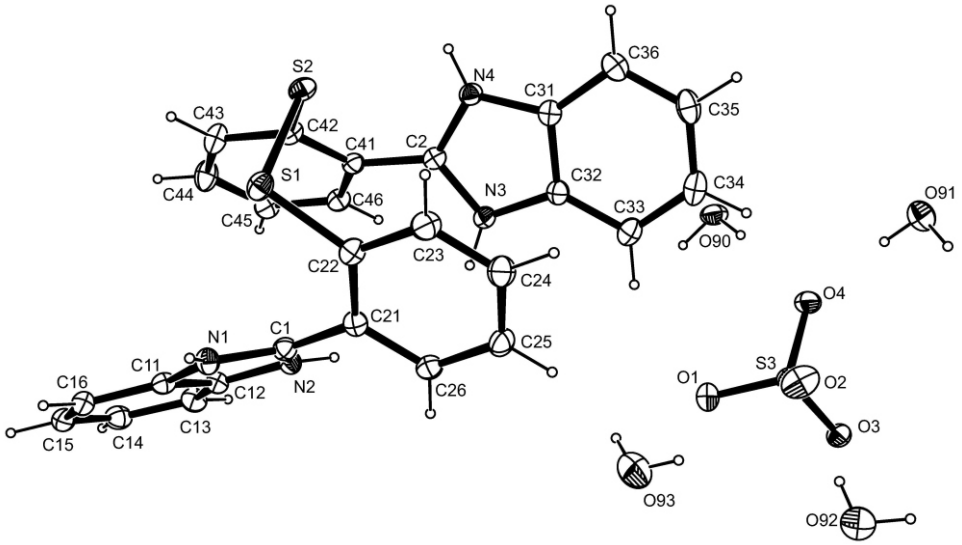

Abstract

$C_{26}H_{28}N_4O_8S_3$, monoclinic, $P12_1/c1$ (no. 14), a = 14.8050(3) Å, b = 15.1570(4) Å, c = 12.3130(3) Å, β = 90.206(1)°, V = 2763.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.102, T = 100 K.

Source of material

The reaction conducted was aimed at synthesizing a vanadium-based coordination compound and the title compound was unintentionally obtained upon reacting 2-(1*H*-benzo[*d*]imidazol-2-yl)benzenethiol with vanadyl sulfate in refluxing methanol/water (*v*/*v* = 1:1). Crystals were obtained upon free evaporation of the solvent.

Experimental details

Carbon-bound H atoms were placed in calculated positions with d(C—H) = 0.95 Å and were included in the refinement in the riding model approximation, with U(H) set to 1.2 U_{eq}(C). The nitrogen-bound H atoms were located from a difference Fourier map and refined freely. The H atoms of the solvent water were located from a difference Fourier map as well and refined using DFIX instructions.

Discussion

Vanadium compounds have been a focus of research in pharmaceutical chemistry due to their possible application as medications for diabetes. To enable targeted uptake as well as secretion of vanadium-containing formulations, finetuning of the solubility as well as hydrophilicity of the compounds under investigation is necessary. In an effort to synthesize a coordination compound of vanadium applying a heterocyclic ligand featuring a thiol group, an unexpected reaction product was isolated. The structure of this compound has been determined at room temperature earlier, but a checkCIF run on the deposited data showed a series of unresolved problems [1]. Comparable molecular set-ups have also been reported earlier in the literature [2,3].

The compound is a twofold-protonated dimer formed upon oxidative coupling of the thiol groups in 2-(1*H*-benzo[*d*]imidazol-2-yl)benzenethiol. Protonation took place on the nitrogen atoms of the five-membered heterocyclic moiety. The compound was isolated as its sulfate salt. The bond length d(S—S) = 2.0511(6) Å, as well as both angles $\angle C_{ar}$–S–S = 100.77(6)° and 100.99(5)°, respectively, are in good agreement with corresponding values in comparable compounds whose data has been deposited with the Cambridge Structural Database [4]. The least-squares planes defined by the aromatic systems in both halfs of the molecule intersect at angles of 50.28(4)° and 44.92(4)°, respectively. The planes defined by the atoms of both benzimidazole moieties enclose an angle of 65.20(3)° while the corresponding angle for the planes defined by phenyl moieties was found at only 28.86(3)°. In the crystal structure, hydrogen bonds between all NH groups as well as all water molecules are present. For two of the NH groups, one O atom of the sulfate anion serves as twofold acceptor while the remaining two NH groups apply the oxygen atom of one water molecule each as acceptor. The protons of the water molecules

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form hydrogen bonds to other water molecules as well as O atoms of the sulfate anion. One of the water molecules spans two of the sulfate anion's O atoms. The descriptor for the hydrogen bonding system in terms of graph-set analysis [5,6] is *DDDDDDDDDDDD* on the unitary level. In total, the components of the crystal structure are connected to a three-dimensional network. The closest intercentroid distance between two π-systems was found at 3.4592(9) Å and is apparent between the five-membered part of a benzimidazole moiety and the six-membered part of its symmetry-generated equivalent.

Table 1. Data collection and handling.

Crystal:	green block, size 0.256 × 0.441 × 0.536 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	3.26 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	56.68°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	48123, 6892
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6306
$N(param)_{refined}$:	407
Programs:	SIR97 [7], SHELXL-97 [8], ORTEP-3 [9], Mercury [10], PLATON [11]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(901)	4*e*	0.053(1)	0.254(2)	0.341(2)	0.033
H(902)	4*e*	0.038(1)	0.235(2)	0.443(1)	0.033
H(911)	4*e*	0.166(1)	0.308(2)	0.011(2)	0.038
H(912)	4*e*	0.130(2)	0.290(2)	0.107(1)	0.038
H(921)	4*e*	0.421(1)	0.246(2)	0.172(2)	0.040
H(922)	4*e*	0.462(2)	0.221(2)	0.084(1)	0.040
H(931)	4*e*	0.369(1)	0.305(2)	0.470(2)	0.057
H(932)	4*e*	0.413(2)	0.310(2)	0.370(1)	0.057
H(711)	4*e*	0.455(2)	0.661(2)	0.876(2)	0.025
H(721)	4*e*	0.315(2)	0.457(2)	0.831(2)	0.023
H(731)	4*e*	0.196(2)	0.442(2)	0.649(2)	0.023
H(741)	4*e*	0.051(2)	0.647(2)	0.591(2)	0.023
H(13)	4*e*	0.3056	0.3970	1.0544	0.023
H(14)	4*e*	0.3567	0.4405	1.2272	0.025
H(15)	4*e*	0.4446	0.5666	1.2500	0.024
H(16)	4*e*	0.4846	0.6558	1.1022	0.022
H(23)	4*e*	0.3204	0.7304	0.5176	0.025
H(24)	4*e*	0.3507	0.6138	0.4002	0.027
H(25)	4*e*	0.3973	0.4772	0.4689	0.024
H(26)	4*e*	0.4157	0.4582	0.6555	0.021
H(33)	4*e*	0.2083	0.3760	0.4292	0.024
H(34)	4*e*	0.1616	0.4131	0.2521	0.028
H(35)	4*e*	0.0731	0.5369	0.2195	0.027
H(36)	4*e*	0.0273	0.6306	0.3609	0.023
H(43)	4*e*	0.1550	0.7302	0.9493	0.026
H(44)	4*e*	0.1303	0.6142	1.0698	0.028
H(45)	4*e*	0.1058	0.4711	1.0048	0.024
H(46)	4*e*	0.1013	0.4453	0.8178	0.020

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*	0.31156(3)	0.75071(3)	0.74548(3)	0.0194(2)	0.0144(2)	0.0215(2)	–0.0031(1)	0.0022(1)	–0.0023(1)
S(2)	4*e*	0.17433(3)	0.74636(2)	0.72262(3)	0.0192(2)	0.0125(2)	0.0199(2)	0.0018(1)	0.0024(1)	0.0016(1)
S(3)	4*e*	0.24505(2)	0.20984(2)	0.27211(3)	0.0166(2)	0.0119(2)	0.0166(2)	0.0007(1)	0.0018(1)	–0.0001(1)
O(1)	4*e*	0.25748(9)	0.21089(9)	0.3910(1)	0.0279(6)	0.0311(7)	0.0179(6)	0.0040(5)	–0.0020(5)	–0.0050(5)
O(2)	4*e*	0.30284(9)	0.27655(8)	0.2219(1)	0.0292(7)	0.0164(6)	0.0407(8)	–0.0044(5)	0.0093(6)	0.0036(5)
O(3)	4*e*	0.27065(8)	0.12052(7)	0.23133(9)	0.0215(5)	0.0126(5)	0.0210(5)	0.0019(4)	–0.0018(4)	–0.0024(4)
O(4)	4*e*	0.14968(8)	0.22544(8)	0.2429(1)	0.0189(6)	0.0266(6)	0.0201(6)	0.0066(5)	0.0009(4)	0.0018(5)
O(90)	4*e*	0.01255(8)	0.25287(8)	0.3874(1)	0.0180(6)	0.0239(6)	0.0234(6)	0.0066(5)	0.0030(5)	0.0033(5)
O(91)	4*e*	0.12019(9)	0.31230(9)	0.0471(1)	0.0282(6)	0.0277(7)	0.0202(6)	0.0002(5)	–0.0018(5)	0.0034(5)
O(92)	4*e*	0.47192(9)	0.23762(9)	0.1470(1)	0.0218(6)	0.0268(7)	0.0315(7)	–0.0060(5)	0.0021(5)	0.0019(5)
O(93)	4*e*	0.4163(1)	0.3055(1)	0.4361(1)	0.0342(8)	0.0437(9)	0.0360(8)	–0.0016(7)	–0.0077(6)	–0.0024(7)
N(1)	4*e*	0.42582(9)	0.61692(9)	0.8895(1)	0.0161(6)	0.0161(6)	0.0170(6)	–0.0034(5)	0.0000(5)	–0.0006(5)
N(2)	4*e*	0.34571(9)	0.49725(9)	0.8669(1)	0.0161(6)	0.0140(6)	0.0157(6)	–0.0019(5)	–0.0012(5)	0.0004(5)
N(3)	4*e*	0.16235(9)	0.48181(9)	0.6096(1)	0.0162(6)	0.0135(6)	0.0153(6)	0.0010(5)	0.0000(5)	–0.0007(5)
N(4)	4*e*	0.08039(9)	0.59934(9)	0.5783(1)	0.0168(6)	0.0144(6)	0.0152(6)	0.0017(5)	0.0011(5)	0.0008(5)
C(1)	4*e*	0.3828(1)	0.5664(1)	0.8172(1)	0.0135(6)	0.0153(7)	0.0175(7)	–0.0003(5)	0.0007(5)	–0.0010(5)
C(2)	4*e*	0.1232(1)	0.5525(1)	0.6542(1)	0.0139(6)	0.0128(6)	0.0162(7)	–0.0008(5)	0.0016(5)	0.0003(5)
C(11)	4*e*	0.4160(1)	0.5792(1)	0.9913(1)	0.0142(7)	0.0161(7)	0.0171(7)	0.0021(5)	0.0013(5)	–0.0003(5)
C(12)	4*e*	0.3644(1)	0.5030(1)	0.9772(1)	0.0140(6)	0.0172(7)	0.0164(7)	0.0010(5)	–0.0012(5)	–0.0011(5)
C(13)	4*e*	0.3408(1)	0.4488(1)	1.0641(1)	0.0186(7)	0.0189(7)	0.0199(7)	–0.0003(6)	–0.0002(6)	0.0024(6)
C(14)	4*e*	0.3716(1)	0.4750(1)	1.1654(1)	0.0212(8)	0.0230(8)	0.0184(7)	0.0040(6)	0.0011(6)	0.0038(6)
C(15)	4*e*	0.4246(1)	0.5513(1)	1.1791(1)	0.0205(7)	0.0240(8)	0.0157(7)	0.0061(6)	–0.0011(6)	–0.0031(6)
C(16)	4*e*	0.4483(1)	0.6047(1)	1.0928(1)	0.0172(7)	0.0182(7)	0.0195(7)	0.0013(6)	–0.0013(6)	–0.0043(6)
C(21)	4*e*	0.3761(1)	0.5824(1)	0.6995(1)	0.0138(6)	0.0171(7)	0.0158(7)	–0.0025(5)	0.0010(5)	0.0002(5)
C(22)	4*e*	0.3469(1)	0.6640(1)	0.6582(1)	0.0169(7)	0.0168(7)	0.0178(7)	–0.0014(6)	0.0030(5)	–0.0003(6)
C(23)	4*e*	0.3388(1)	0.6750(1)	0.5462(1)	0.0241(8)	0.0209(8)	0.0182(7)	0.0024(6)	0.0033(6)	0.0040(6)
C(24)	4*e*	0.3572(1)	0.6058(1)	0.4763(1)	0.0251(8)	0.0277(9)	0.0155(7)	0.0020(7)	0.0034(6)	0.0014(6)
C(25)	4*e*	0.3852(1)	0.5247(1)	0.5171(1)	0.0195(7)	0.0234(8)	0.0174(7)	0.0014(6)	0.0041(6)	–0.0030(6)
C(26)	4*e*	0.3955(1)	0.5133(1)	0.6279(1)	0.0153(7)	0.0184(7)	0.0191(7)	0.0011(6)	0.0018(6)	–0.0004(6)
C(31)	4*e*	0.0930(1)	0.5582(1)	0.4788(1)	0.0155(7)	0.0158(7)	0.0160(7)	–0.0031(5)	0.0016(5)	0.0002(5)
C(32)	4*e*	0.1456(1)	0.4834(1)	0.4984(1)	0.0154(7)	0.0155(7)	0.0160(7)	–0.0026(5)	0.0002(5)	–0.0009(5)
C(33)	4*e*	0.1726(1)	0.4269(1)	0.4154(1)	0.0208(7)	0.0183(7)	0.0209(8)	–0.0017(6)	0.0027(6)	–0.0040(6)
C(34)	4*e*	0.1444(1)	0.4494(1)	0.3115(1)	0.0255(8)	0.0252(8)	0.0181(7)	–0.0079(7)	0.0049(6)	–0.0059(6)
C(35)	4*e*	0.0911(1)	0.5242(1)	0.2920(1)	0.0250(8)	0.0272(8)	0.0145(7)	–0.0093(7)	0.0009(6)	0.0018(6)
C(36)	4*e*	0.0638(1)	0.5802(1)	0.3746(1)	0.0200(7)	0.0207(8)	0.0180(7)	–0.0042(6)	–0.0008(6)	0.0043(6)
C(41)	4*e*	0.1264(1)	0.5725(1)	0.7709(1)	0.0139(6)	0.0153(7)	0.0146(7)	0.0016(5)	0.0011(5)	–0.0005(5)
C(42)	4*e*	0.1443(1)	0.6577(1)	0.8103(1)	0.0177(7)	0.0143(7)	0.0171(7)	0.0007(5)	0.0036(5)	0.0008(5)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(43)	4*e*	0.1446(1)	0.6724(1)	0.9221(1)	0.0276(8)	0.0178(7)	0.0184(7)	–0.0029(6)	0.0044(6)	–0.0041(6)
C(44)	4*e*	0.1299(1)	0.6034(1)	0.9938(1)	0.0314(9)	0.0246(8)	0.0146(7)	–0.0027(7)	0.0047(6)	–0.0017(6)
C(45)	4*e*	0.1147(1)	0.5184(1)	0.9553(1)	0.0217(8)	0.0204(8)	0.0170(7)	–0.0006(6)	0.0037(6)	0.0030(6)
C(46)	4*e*	0.1124(1)	0.5031(1)	0.8443(1)	0.0170(7)	0.0145(7)	0.0179(7)	–0.0002(5)	0.0019(5)	0.0006(5)

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