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Crystal structure of bis(2,6-diaminopyridinium) diaqua-bis-(2,6-pyridinedicarboxylato)-bis(2,6-pyridinedicarboxylato)-dibismuthate(III) tetrahydrate, $(C_{28}H_{16}O_{18}N_4Bi_2)(C_5H_8N_3)_2 \cdot 4H_2O$

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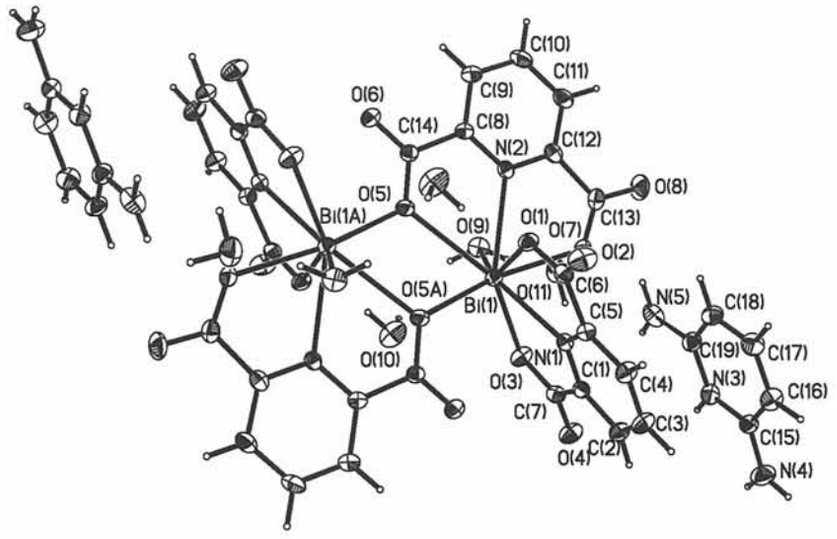

Abstract

$C_{38}H_{40}Bi_2N_{10}O_{22}$, triclinic, $P\bar{1}$ (No. 2), $a = 9.699(1)$ Å, $b = 10.500(1)$ Å, $c = 10.890(1)$ Å, $\alpha = 85.587(3)°$, $\beta = 88.128(3)°$, $\gamma = 84.257(3)°$, $V = 1099.9$ Å^3, $Z = 1$, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.061$, $T = 295$ K.

Source of material

The title compound was synthesised by the reaction between ligand LH_2, $[H_2pyda]^{2+}[pydc]^{2-}$, (pyda = 2,6-pyridinediamine and H_2pydc = 2,6-pyridinedicarboxylic acid) [1], and bismuth subnitrate $[4BiNO_3(OH)_2 \cdot BiOOH]$ in aqueous solution. After two weeks, colorless crystals were isolated.

Experimental details

There is a positive residual density of 1.31 e·Å^{-3} near the N5 center (distance 0.36 Å), which can be the result of several factors that contribute to the bias of the data. Also, a refinement of a model considering a possible disordering of N5 failed. This together with the relative small displacement factor of N5 do not support the hypothesis that the residual electron density near N5 is the consequence of disordering.

Discussion

Bismuth complexes are of interest in the treatment of gastric ulcer [2], and may also be useful for the treatment of other diseases. Bi(III) exhibits a highly variable coordination number (three-ten) and often an irregular coordination geometry [3]. The coordination chemistry of Bi(III) with carboxylates and aminocarboxylates is dominated by intermolecular interactions which leads to polymeric structures [3]. Continuing the synthesis of a novel self-assembling pyridine containing system ligand LH_2 [1], we become interested in investigating the influence of the counter ion $[H_2pyda]^{2+}$ in the complexation process and succeeded in reporting some of them [4-6]. Here we report the crystal structure of a novel Bi(III) complex. The molecular structure consists of two metal fragments linked via the central four-membered Bi_2O_2 ring. The five Bi—O bonds are in the range 2.327(3) Å to 2.589(3) Å and the two Bi—N1 and Bi—N2 distances are 2.435(3) Å and 2.555(3) Å, respectively. It is interesting to note that, the existence of a stereochemically active lone pair on the Bi(III) atoms. These distances are in agreement with a previous report [7]. There is a significant difference between the N—C bonds in the 2,6-diaminopyridinium cation. However, such a difference is not uncommon in published structures containing this cationic fragment in the presence of heavy ions [8]. Discussing the self-assembled binuclear complex of Bi(III), the extensive intermolecular hydrogen bonding between coordinated and uncoordinated water molecules, two $[Hpyda]^+$ and one $[Bi_2(pydc)_4(H_2O)_2]^{2-}$ species has to be mentioned. The intermolecular forces existing between anionic and cationic units in the Bi(III) complex consist of both H-bonding and ion-pairing.

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Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.17 × 0.24 × 0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	80.89 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	60.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24752, 6425
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5386
$N(param)_{refined}$:	331
Programs:	SHELXTL [9], SADABS [10]

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

Atom	Site	x	y	z	U_{iso}
H(9A)	2*i*	0.6268	0.6808	0.3959	0.06
H(9B)	2*i*	0.5878	0.6135	0.3000	0.06
H(10A)	2*i*	0.7895	0.6069	0.6247	0.06
H(10B)	2*i*	0.6677	0.6197	0.5772	0.06
H(11A)	2*i*	0.3748	0.5470	0.2514	0.06
H(11B)	2*i*	0.3786	0.5969	0.1471	0.06
H(3N)	2*i*	0.3574	0.1206	0.2271	0.06
H(4A)	2*i*	0.2908	–0.0731	0.2692	0.06
H(4B)	2*i*	0.3798	–0.1912	0.2392	0.06
H(5A)	2*i*	0.4040	0.3391	0.1853	0.06
H(5B)	2*i*	0.5377	0.3670	0.1227	0.06
H(2)	2*i*	0.6153	–0.0015	0.4529	0.06
H(3)	2*i*	0.8126	–0.1337	0.3971	0.06
H(4)	2*i*	1.0134	–0.0430	0.3356	0.06
H(9)	2*i*	1.1049	0.8211	0.1260	0.06
H(10)	2*i*	1.0054	0.8080	–0.0612	0.06
H(11)	2*i*	0.8508	0.6540	–0.0817	0.06
H(16)	2*i*	0.6106	–0.1709	0.1347	0.06
H(17)	2*i*	0.7639	–0.0292	0.0593	0.06
H(18)	2*i*	0.7086	0.1900	0.0643	0.06

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}
Bi(1)	2*i*	0.83147(1)	0.44620(1)	0.38360(1)	0.02483(7)	0.02614(7)	0.02813(7)	–0.00382(5)	–0.00108(5)	–0.00110(5)
O(1)	2*i*	1.0432(2)	0.3312(2)	0.3095(2)	0.027(1)	0.033(1)	0.037(1)	–0.008(1)	0.006(1)	–0.002(1)
O(2)	2*i*	1.1662(3)	0.1444(3)	0.2828(3)	0.025(1)	0.043(2)	0.067(2)	0.006(1)	0.016(1)	–0.001(1)
O(3)	2*i*	0.6059(2)	0.3772(2)	0.4415(2)	0.026(1)	0.028(1)	0.055(2)	–0.002(1)	0.006(1)	–0.004(1)
O(4)	2*i*	0.4694(3)	0.2198(3)	0.4753(3)	0.026(1)	0.040(2)	0.067(2)	–0.007(1)	0.013(1)	–0.007(1)
O(5)	2*i*	1.0135(3)	0.6120(2)	0.4273(2)	0.038(1)	0.032(1)	0.026(1)	–0.011(1)	–0.004(1)	0.006(1)
O(6)	2*i*	1.1546(3)	0.7558(3)	0.3537(2)	0.043(2)	0.044(2)	0.038(2)	–0.021(1)	–0.002(1)	–0.001(1)
O(7)	2*i*	0.7465(3)	0.4116(2)	0.1925(2)	0.045(2)	0.035(1)	0.030(1)	–0.013(1)	–0.008(1)	–0.002(1)
O(8)	2*i*	0.7090(3)	0.4657(3)	–0.0043(3)	0.071(2)	0.060(2)	0.041(2)	–0.016(2)	–0.029(2)	–0.004(1)
O(9)	2*i*	0.6557(3)	0.6433(2)	0.3322(2)	0.032(1)	0.039(1)	0.041(2)	0.004(1)	–0.001(1)	0.000(1)
O(10)	2*i*	0.7217(3)	0.5621(3)	0.6150(3)	0.039(2)	0.050(2)	0.088(3)	–0.004(1)	–0.018(2)	0.002(2)
O(11)	2*i*	0.4146(3)	0.6084(3)	0.2151(3)	0.052(2)	0.058(2)	0.050(2)	–0.010(2)	–0.013(1)	–0.010(2)
N(1)	2*i*	0.8210(3)	0.2155(2)	0.3806(2)	0.022(1)	0.025(1)	0.023(1)	0.002(1)	0.000(1)	–0.002(1)
N(2)	2*i*	0.9202(3)	0.5891(3)	0.2037(2)	0.027(2)	0.027(1)	0.024(1)	0.001(1)	–0.002(1)	–0.003(1)
N(3)	2*i*	0.4349(3)	0.0924(3)	0.1941(3)	0.023(2)	0.043(2)	0.041(2)	–0.003(1)	0.005(1)	–0.011(1)
N(4)	2*i*	0.3666(4)	–0.1087(4)	0.2386(4)	0.049(2)	0.050(2)	0.068(3)	–0.020(2)	0.014(2)	–0.003(2)
N(5)	2*i*	0.4828(3)	0.3141(3)	0.1522(3)	0.020(2)	0.049(2)	0.036(2)	0.022(1)	0.003(1)	–0.008(1)
C(1)	2*i*	0.7042(3)	0.1646(3)	0.4159(3)	0.026(2)	0.028(2)	0.025(2)	–0.004(1)	–0.000(1)	–0.001(1)
C(2)	2*i*	0.6965(4)	0.0331(3)	0.4259(3)	0.026(2)	0.031(2)	0.040(2)	–0.005(2)	0.002(2)	–0.001(2)
C(3)	2*i*	0.8147(4)	–0.0450(3)	0.3939(4)	0.040(2)	0.024(2)	0.056(3)	–0.005(2)	0.001(2)	–0.002(2)
C(4)	2*i*	0.9340(4)	0.0088(3)	0.3563(4)	0.029(2)	0.024(2)	0.047(2)	0.004(1)	0.003(2)	–0.003(2)
C(5)	2*i*	0.9340(3)	0.1403(3)	0.3507(3)	0.024(2)	0.026(2)	0.029(2)	–0.001(1)	–0.001(1)	0.000(1)
C(6)	2*i*	1.0587(4)	0.2096(3)	0.3116(3)	0.028(2)	0.033(2)	0.028(2)	–0.000(2)	0.003(1)	–0.004(1)
C(7)	2*i*	0.5841(3)	0.2598(3)	0.4472(3)	0.022(2)	0.033(2)	0.031(2)	–0.002(1)	0.001(1)	–0.000(2)
C(8)	2*i*	1.0075(3)	0.6778(3)	0.2158(3)	0.021(2)	0.026(2)	0.028(2)	0.002(1)	0.002(1)	0.002(1)
C(9)	2*i*	1.0426(4)	0.7612(4)	0.1163(3)	0.043(2)	0.034(2)	0.035(2)	–0.009(2)	0.003(2)	0.005(2)
C(10)	2*i*	0.9840(4)	0.7527(4)	0.0054(3)	0.056(3)	0.048(2)	0.026(2)	–0.010(2)	0.005(2)	0.009(2)
C(11)	2*i*	0.8920(4)	0.6618(4)	–0.0074(3)	0.046(2)	0.047(2)	0.025(2)	–0.005(2)	–0.004(2)	0.003(2)
C(12)	2*i*	0.8633(4)	0.5814(3)	0.0959(3)	0.032(2)	0.035(2)	0.026(2)	0.001(2)	–0.003(2)	–0.003(2)
C(13)	2*i*	0.7649(4)	0.4790(3)	0.0924(3)	0.038(2)	0.031(2)	0.035(2)	–0.000(2)	–0.008(2)	–0.007(2)
C(14)	2*i*	1.0650(3)	0.6830(3)	0.3414(3)	0.026(2)	0.025(2)	0.027(2)	–0.001(1)	0.001(1)	–0.000(1)
C(15)	2*i*	0.4641(4)	–0.0367(3)	0.1908(3)	0.036(2)	0.035(2)	0.032(2)	–0.010(2)	–0.002(2)	–0.002(2)
C(16)	2*i*	0.5884(4)	–0.0830(4)	0.1384(4)	0.036(2)	0.032(2)	0.051(2)	0.006(2)	–0.004(2)	–0.000(2)
C(17)	2*i*	0.6788(4)	0.0013(4)	0.0930(4)	0.030(2)	0.053(2)	0.050(2)	–0.002(2)	0.011(2)	–0.009(2)
C(18)	2*i*	0.6466(4)	0.1333(4)	0.0964(4)	0.027(2)	0.046(2)	0.045(2)	–0.012(2)	0.004(2)	–0.004(2)
C(19)	2*i*	0.5209(4)	0.1792(4)	0.1473(3)	0.032(2)	0.036(2)	0.040(2)	–0.008(2)	0.000(2)	–0.005(2)

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