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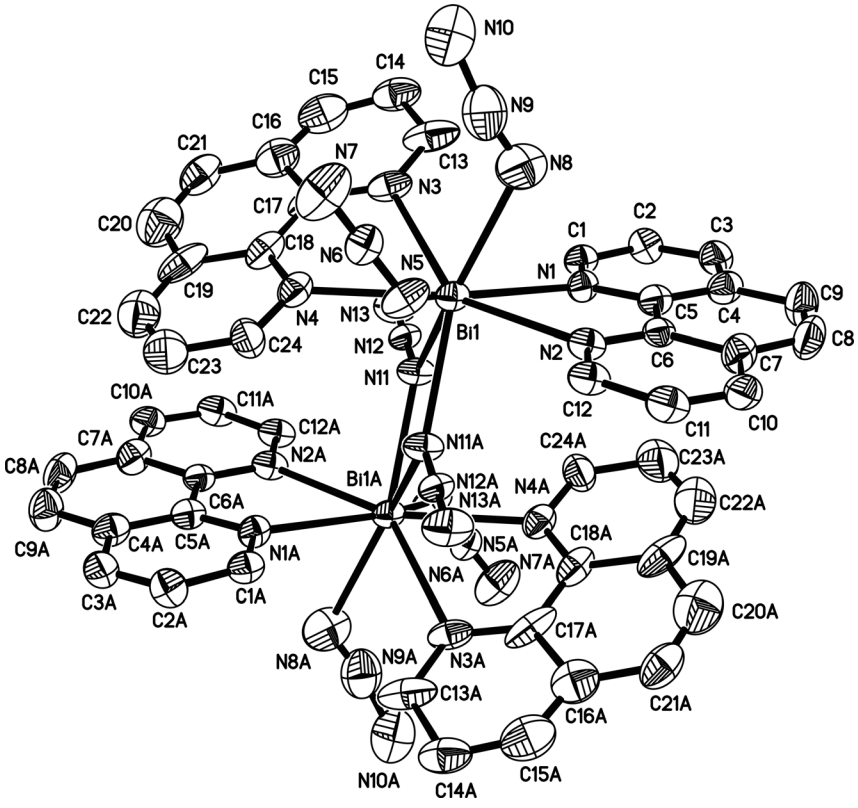
Crystal structure of bis(μ$_2$-azido-κ^2*N:N*)-tetrakis(azido-κ^1*N*)-tetrakis(1,10-phenanthroline-κ^2*N,N′*)dibismuth(III), $C_{48}H_{32}N_{26}Bi_2$



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Abstract

$C_{48}H_{32}N_{26}Bi_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.781(5) Å, b = 11.667(6) Å, c = 11.973(7) Å, α = 83.816(10)°, β = 74.471(10)°, γ = 66.120(8)°, V = 1203.7 (11) Å^3, Z = 1, $R_{gt}(F)$ = 0.0435, w$R_{ref}(F^2)$ = 0.1035, T = 293 K.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.26 × 0.21 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	7.37 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	25.1°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7846, 4254, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3351
N(param)$_{refined}$:	343
Programs:	Bruker [1], Olex2 [2, 3]

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Bi1	0.14456 (3)	0.89825 (3)	0.83876 (3)	0.04363 (14)
C1	0.3471 (10)	1.0973 (9)	0.7947 (8)	0.052 (2)
H1	0.3842 (10)	1.0490 (9)	0.8555 (8)	0.062 (3)*
C2	0.4088 (11)	1.1824 (10)	0.7426 (9)	0.060 (3)
H2	0.4865 (11)	1.1913 (10)	0.7672 (9)	0.072 (3)*
C3	0.3542 (11)	1.2531 (10)	0.6546 (10)	0.066 (3)
H3	0.3973 (11)	1.3090 (10)	0.6169 (10)	0.079 (3)*
C4	0.2337 (11)	1.2432 (10)	0.6195 (9)	0.059 (3)
C5	0.1796 (10)	1.1533 (9)	0.6751 (8)	0.051 (2)
C6	0.0584 (9)	1.1373 (9)	0.6420 (7)	0.046 (2)
C7	−0.0054 (12)	1.2188 (10)	0.5573 (9)	0.063 (3)
C8	0.0547 (14)	1.3070 (10)	0.5043 (10)	0.076 (3)
H8	0.0109 (14)	1.3597 (10)	0.4482 (10)	0.091 (4)*
C9	0.1713 (13)	1.3181 (11)	0.5311 (10)	0.075 (3)
H9	0.2117 (13)	1.3750 (11)	0.4917 (10)	0.090 (4)*
C10	−0.1298 (11)	1.2039 (10)	0.5307 (9)	0.064 (3)
H10	−0.1787 (11)	1.2566 (10)	0.4768 (9)	0.076 (3)*
C11	−0.1783 (11)	1.1131 (11)	0.5833 (8)	0.064 (3)
H11	−0.2595 (11)	1.1033 (11)	0.5650 (8)	0.077 (4)*
C12	−0.1066 (10)	1.0353 (10)	0.6644 (8)	0.056 (3)
H12	−0.1392 (10)	0.9723 (10)	0.6984 (8)	0.067 (3)*
C13	0.5433 (12)	0.7864 (11)	0.8344 (14)	0.096 (5)
H13	0.5462 (12)	0.8319 (11)	0.7657 (14)	0.115 (6)*
C14	0.6823 (13)	0.7326 (11)	0.8829 (13)	0.086 (3)
H14	0.7749 (13)	0.7410 (11)	0.8479 (13)	0.103 (4)*
C15	0.6581 (17)	0.6697 (13)	0.9846 (14)	0.103 (4)
H15	0.7429 (17)	0.6374 (13)	1.0168 (14)	0.124 (5)*
C16	0.5454 (16)	0.6468 (12)	1.0433 (13)	0.087 (4)
C17	0.4161 (14)	0.7014 (10)	0.9890 (12)	0.079 (4)
C18	0.2834 (14)	0.6792 (9)	1.0445 (9)	0.063 (3)
C19	0.2739 (16)	0.6045 (10)	1.1502 (12)	0.084 (4)
C20	0.401 (2)	0.5616 (14)	1.1937 (15)	0.116 (5)
H20	0.397 (2)	0.5170 (14)	1.2629 (15)	0.139 (6)*
C21	0.5253 (15)	0.5779 (11)	1.1469 (11)	0.081 (3)
H21	0.6068 (15)	0.5428 (11)	1.1825 (11)	0.098 (4)*
C22	0.1409 (19)	0.5832 (13)	1.1887 (13)	0.097 (4)
H22	0.1316 (19)	0.5356 (13)	1.2556 (13)	0.117 (5)*
C23	0.0280 (18)	0.6241 (12)	1.1394 (12)	0.102 (5)
H23	−0.0591 (18)	0.6058 (12)	1.1680 (12)	0.122 (6)*
C24	0.0436 (14)	0.6966 (10)	1.0415 (10)	0.072 (3)
H24	−0.0377 (14)	0.7284 (10)	1.0056 (10)	0.087 (4)*
N1	0.2352 (8)	1.0808 (7)	0.7616 (6)	0.0478 (18)
N2	0.0086 (8)	1.0484 (7)	0.6951 (6)	0.050 (2)
N3	0.4181 (8)	0.7697 (8)	0.8881 (8)	0.062 (2)
N4	0.1632 (10)	0.7236 (7)	0.9958 (7)	0.058 (2)
N5	0.0269 (9)	0.7798 (8)	0.7840 (8)	0.068 (3)
N6	0.0867 (9)	0.6760 (9)	0.7631 (7)	0.054 (2)
N7	0.1408 (14)	0.5752 (11)	0.7396 (12)	0.107 (4)
N8	0.3295 (14)	0.8334 (12)	0.6514 (9)	0.101 (3)
N9	0.3992 (16)	0.7350 (14)	0.6343 (11)	0.108 (4)
N10	0.5003 (19)	0.6176 (15)	0.5956 (15)	0.162 (6)
N11	0.1249 (8)	1.0022 (7)	1.0353 (6)	0.0491 (19)
N12	0.2372 (8)	0.9873 (6)	1.0674 (6)	0.0463 (18)
N13	0.3426 (9)	0.9750 (9)	1.0968 (8)	0.072 (3)

1 Source of material

The titled compound $Bi_2(\mu_2\text{–}N_3)_2(C_{12}H_8N_2)_4(N_3)_4$ was prepared through the hydrothermal method. The mixture of $Bi(NO_3)_3{\cdot}5H_2O$ (0.36 g), phen ($C_{12}H_8N_2$, 0.08 g), NaN_3 (0.29 g) and H_2O (5.2 mL) was transferred into a 50 mL Teflon-lined stainless steel vessel and heated at 140 °C for 130 h. After cooling to RT, the block yellow crystals were obtained, washed with distilled water and dried at RT (yield: 76 % based on $Bi(NO_3)_3{\cdot}5H_2O$).

2 Experimental details

The H atoms of the C atoms from the organic ligands were positioned geometrically and refined using a riding model, with C–H = 0.93 Å, with U_{iso}(H) = 1.2 times U_{eq}(C). Two restrictive refinements, isor and delu, were applied to deal with partially distorted nitrogen and carbon atoms in the structure.

3 Comment

It is an effective way to construct novel compounds by using linear azide anions with flexible coordination modes and various metal cations [4, 5]. The N atom at both ends of the azide ion can coordinate directly with the metal cation or link as a bridge atom with two/three metal cations to form a compound with new structural features [6]. Herein, using two types of nitrogen-containing ligands, azide (N_3^-) and 1,10-phenanthroline (phen), we prepared a new binuclear coordination compound $Bi_2(\mu_2\text{–}N_3)_2(C_{12}H_8N_2)_4(N_3)_4$ based on Bi^{3+} cations by means of hydrothermal method. Within its molecular structure (Figure), each Bi^{3+} cation is coordinated with eight surrounding nitrogen atoms, of which four nitrogen atoms are from two different phen ligands and four N atoms belong to four surrounding azide anions, resulting in the formation of a $\{BiN_8\}$ hexagonal bipyramidal geometric configuration. The distances of Bi–N bonds are in the range of 2.356(8)–2.689(7) Å. The bond angles of N–Bi–N are in the scope of 61.9(3)–152.7(3)°. The mentioned parameters of bond lengths and angles are consistent with those of previously known Bi^{3+}-containing complexes [7–10] and fall within their normal range. It is worth noting that the azide ions exhibit two kinds of coordination modes: the single coordination and the bridging coordination of the terminal N atoms. The two Bi^{3+} cations are bridged by two terminal N atoms of different azide groups to generate a binuclear

structure. The flexible coordination modes of the azide anions in the title compound can be observed in the compounds that we reported previously. The distance of Bi···Bi is 4.386 Å. In addition, there are π–π stacking interactions between phenanthroline molecules in its packing scheme [centroid-to–centroid distances: 3.808(6) Å(*Cg*1-*Cg*1^{i}, *i*: –*x*, 2–*y*, 1–*z*), 5.479(8) Å(*Cg*2–*Cg*3^{ii}, *ii*: 1–*x*, 1–*y*, 2–*z*) and 3.504(8) Å(*Cg*2-*Cg*4^{ii}, *ii*: 1–*x*, 1–*y*, 2–*z*), *Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of 6–MRs involving atoms N(2)/C(6),C(10)–C(12); N(1)/C(1)–C(5); N(3)/C(13)–C(17) and C(16)–C(20), respectively].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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