Refinement of the crystal structure of tris(nitrato-*O,O'*)-bis(1,10-phenanthroline)bismuth(III), $Bi(C_{12}H_8N_2)_2(NO_3)_3$, *at 110 K*

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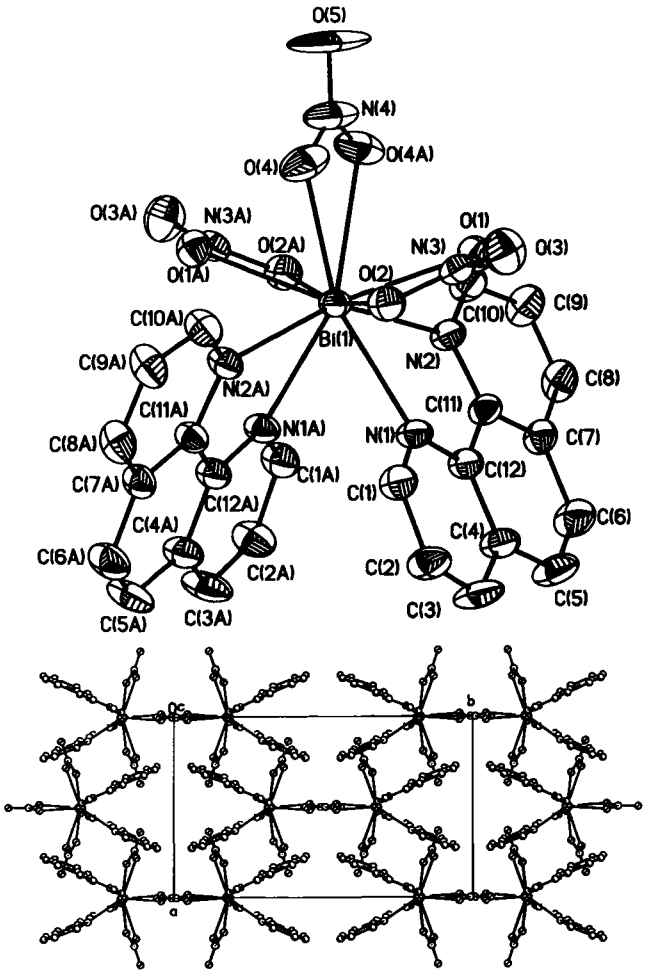

Abstract

$C_{24}H_{16}BiN_7O_9$, monoclinic, *C*12/*c*1 (No. 15), $a = 10.999(2)$ Å, $b = 17.813(4)$ Å, $c = 12.993(3)$ Å, $\beta = 100.728(5)°$, $V = 2501.2$ Å^3, $Z = 4$, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.061$, $T = 110$ K.

Source of material

a) The complex $[Bi()_2(NO_3)_3]$ was prepared by dissolving 0.266 g (1 mmol) bismuth (I) nitrate in distillation water and adding mixture alcoholic solution of 1,10-phenanthroline(phen). (0.4 g, 2 mmol). The resulting solution was stirred for 4 h at room temperature, then it was allowed to stand for 2-3 days in refrigerator. white crystals of the desired product precipitated, which were filtered off, and washed with aceton and ether and air dried (0.500 g, yield 60%), mp 460 K. Elemental analyses were consistent with the stoichiometry $C_{24}H_{16}BiN_6O_9$ (found: C, 37.1%; H, 2.24%; N, 13.05%; calculated: C, 38.2%; H, 2.1%; N, 13.0%).

b) Branched tube method: 1,10-Phenanthroline (0.2 g ,1 mmol) was placed in one arm of the branched tube and a mixture of bismuth (III) nitrate (0.18 g, 0.5 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60 °C while the other was at ambient temperature. After 10 d, white crystals (mp 187 °C) had been deposited in the cooler arm.

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer.

Experimental details

Lower symmetry space groups that break the 2-fold axis were tested. No indications of lower symmetry were observed. Thus, the refinement was done using the previously determined space group in [1]. We have not clear explanations for the extremely high U_{ij} values for the positions N4 (U_{33}), O5 (U_{11}) and other correlated atom positions, but it is possible that at the short-range level there is a break of the 2-fold symmetry.

Discussion

Bismuth complexes are of interest in the treatment of gastric ulcer [2,3]. In the last few years, there is interest in the study of magnetic, electronic and optoelectronic properties of main group metal complexes [1,4,5]. An issue frequently discussed in considering the coordination and stereoactive of heavy metals is that of the stereochemical activity of valence shell lone electron pairs (see for example [6]). Since the presence of lone pair is not directly detected but is inferred on the basis of the spatial distribution of atoms assumed to be donors to the central atom, the identification of these donor atoms is fundamental to the analysis of any particular system. Interestingly, this alone is not a straightforward process. The coordination chemistry of bismuth(III) is disproportionately sparse when compared with that of other metals [1-4]. Attempts to isolate the mixed-ligands complexes of perchlorate and acetate ligands $(phen)Bi(NO_3)_n(ClO_4)_m]$ (n+m=3) and $[(phen)Bi(NO_3)_n(CH_3COO)_m]$ were not successful, and instead of these complexes, the $Bi(phen)_2(NO_3)_3$ compound was isolated. Determination of the structure of $Bi(phen)_2(NO_3)_3$ by X-ray crystallography at low temperature (110 K) showed the complex in the solid state to be a monomeric species (upper figure). The coordination number of bismuth atoms is ten. Each bismuth atom is coordinated by four nitrogen atoms of the two 1,10-phenantroline ligands and six oxygen atoms of the three nitrate anions. The arrangement of the two 1,10-phenanthroline ligands and three NO_3^- anions suggests a regular environment around the bismuth(III) ion, and because there is no gap in this arrangement, it is possible that the lone pair of electrons on bismuth(III) is stereoinactive.

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The difference between the reported room temperature structure [1] and the present one (110 K) is not significant. However, in the present study the atomic parameters were determined with better accuracy.

Finally, we note that throughout the arrays of species of diverse symmetries found in the literature, with diverse concomitant, crystal packing, etc., it is difficult to discern any effects which might be consistently attributable to the existence/influence of 'stereochemically active lone pairs'. The striking point is that in the title compound, there is a π-π stacking interaction (charge-transfer arrays [2,3]) between the parallel aromatic rings belonging to adjacent chains (lower figure).

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.20 × 0.20 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	71.19 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	59.14°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9740, 3432
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2992
$N(param)_{refined}$:	187
Programs:	SHELXTL-plus [7], SHELXL-97 [8], SADABS [9]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	8*f*	0.3409	0.1911	0.0837	0.041
H(2A)	8*f*	0.2614	0.0711	0.0771	0.050
H(3A)	8*f*	0.2444	0.0098	0.2302	0.057
H(5A)	8*f*	0.2559	0.0178	0.4272	0.057
H(6A)	8*f*	0.3063	0.0837	0.5778	0.052
H(8A)	8*f*	0.3916	0.2025	0.6720	0.046
H(9A)	8*f*	0.4727	0.3198	0.6626	0.049
H(10A)	8*f*	0.5080	0.3652	0.5039	0.044

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)	4*e*	1/2	0.32044(1)	1/4	0.0358(1)	0.01981(9)	0.02721(9)	0	0.01136(7)	0
O(1)	8*f*	0.2783(2)	0.3680(2)	0.2498(2)	0.036(1)	0.036(1)	0.029(1)	–0.002(1)	0.009(1)	–0.005(1)
O(2)	8*f*	0.3104(3)	0.3346(1)	0.0969(2)	0.043(2)	0.033(1)	0.026(1)	–0.001(1)	0.009(1)	–0.001(1)
O(3)	8*f*	0.1341(3)	0.3828(2)	0.1124(3)	0.038(2)	0.058(2)	0.050(2)	0.004(1)	0.002(1)	0.000(2)
O(4)	8*f*	0.4834(3)	0.4552(2)	0.1653(3)	0.046(2)	0.032(2)	0.064(2)	–0.005(1)	–0.005(2)	0.017(1)
O(5)	4*e*	1/2	0.5598(2)	1/4	0.083(4)	0.011(2)	0.192(8)	0	–0.052(5)	0
N(1)	8*f*	0.3693(3)	0.2036(2)	0.2350(2)	0.042(2)	0.021(1)	0.025(1)	–0.005(1)	0.010(1)	–0.003(1)
N(2)	8*f*	0.4441(3)	0.2785(2)	0.4187(2)	0.043(2)	0.027(1)	0.023(1)	–0.008(1)	0.013(1)	–0.004(1)
N(3)	8*f*	0.2375(3)	0.3620(2)	0.1518(2)	0.034(2)	0.025(1)	0.031(2)	–0.006(1)	0.007(1)	0.001(1)
N(4)	4*e*	1/2	0.4915(3)	1/4	0.034(3)	0.020(2)	0.107(5)	0	–0.016(3)	0
C(1)	8*f*	0.3336(4)	0.1673(2)	0.1459(3)	0.049(2)	0.032(2)	0.025(2)	–0.005(2)	0.013(2)	–0.002(1)
C(2)	8*f*	0.2853(4)	0.0949(2)	0.1414(3)	0.064(3)	0.032(2)	0.031(2)	–0.014(2)	0.014(2)	–0.011(2)
C(3)	8*f*	0.2732(5)	0.0589(2)	0.2318(3)	0.083(3)	0.024(2)	0.038(2)	–0.021(2)	0.016(2)	–0.007(2)
C(4)	8*f*	0.3054(4)	0.0978(2)	0.3276(3)	0.056(2)	0.024(2)	0.031(2)	–0.008(2)	0.015(2)	–0.002(1)
C(5)	8*f*	0.2885(5)	0.0659(2)	0.4258(3)	0.083(3)	0.028(2)	0.035(2)	–0.020(2)	0.022(2)	0.001(2)
C(6)	8*f*	0.3193(4)	0.1049(2)	0.5153(3)	0.065(3)	0.037(2)	0.031(2)	–0.009(2)	0.019(2)	0.004(2)
C(7)	8*f*	0.3715(4)	0.1781(2)	0.5164(3)	0.040(2)	0.032(2)	0.024(2)	–0.004(2)	0.011(1)	0.001(1)
C(8)	8*f*	0.4038(4)	0.2214(2)	0.6079(3)	0.044(2)	0.049(2)	0.023(2)	–0.007(2)	0.010(2)	–0.003(2)
C(9)	8*f*	0.4527(4)	0.2905(3)	0.6026(3)	0.051(2)	0.050(2)	0.025(2)	–0.018(2)	0.013(2)	–0.011(2)
C(10)	8*f*	0.4730(4)	0.3178(2)	0.5064(3)	0.046(2)	0.036(2)	0.029(2)	–0.013(2)	0.014(2)	–0.009(2)
C(11)	8*f*	0.3909(3)	0.2104(2)	0.4219(3)	0.035(2)	0.025(2)	0.024(2)	–0.006(1)	0.009(1)	–0.000(1)
C(12)	8*f*	0.3547(4)	0.1697(2)	0.3257(3)	0.041(2)	0.024(2)	0.024(2)	–0.004(1)	0.011(1)	–0.001(1)

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References

1. Barbour, L. J.; Belfield, S. J.; Junk, P. C.; Smith. M. K.: Bidentate Nitrogen Base Adducts of Bismuth(II) Nitrate. Aust. J. Chem. **51** (1998) 337-342.
2. Grenwood, N. N.; Earnshaw, A.: Chemistry of the Elements, Pergamon Press, Oxford, 1984, pp. 235-236.
3. Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. (Eds): Comprehensive Coordination Chemistry, Vols 1-7, Pergamon: London 1987.
4. Bowmaker, G. A.; Hannaway, F. M. M.; Junk, P. C.; Lee, A. M.; Skelton, B. W.; White, A. H.: Synthetic, Structural and Vibrational Spectroscopic Studies in Bismuth(III) Halides. Aust. J. Chem. **51** (1998) 325-330.
5. Morsali, A.; Tadjarodi, A.; Mohammadi, R.; Mahjoub A. R.: Crystal structure of bis(4,4'-bitiazole)bismuth(III) trinitrate hemihydrate, $Bi(C_6H_4N_2S_2)_2(NO_3)_2 \cdot 0.5H_2O$. Z. Kristallogr. NCS **216** (2001) 379-380.
6. Shimoni-Livny, L.; Glusker, J. P.; Bock, C. W.: Lone pair functionality in divalent lead compounds. Inorg. Chem. **37** (1998) 1853-1867.
7. Sheldrick G. M.: SHELXTL-plus, Version 5.o. Software Reference Manual, Siemens Industrial Automation, Inc., Madison, USA 1995.
8. Sheldrick G. M.: SHELXTL-97. A Program for Refining Crystal Structures. Version 5.1o, Bruker AXS Inc., Madison, WI-53719, USA 1997.
9. Sheldrick G. M.: SADABS, Bruker AXS Inc., Madison, WI-53719, USA 1997.