Refinement of the crystal structure of *trans*-bis(1,10-phenanthroline)-bismuth(III) tribromide, $C_{24}H_{16}BiBr_3N_4$

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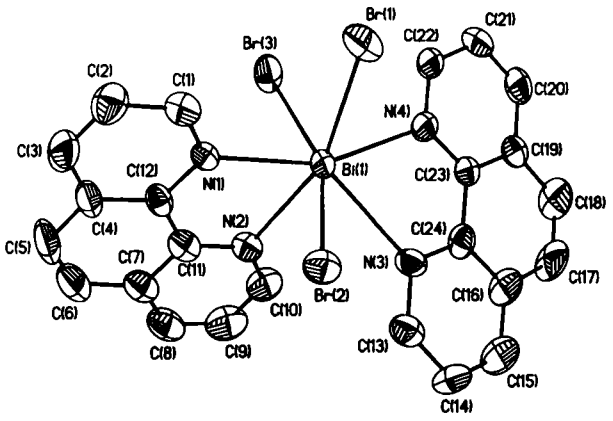

Abstract

$C_{24}H_{16}BiBr_3N_4$, monoclinic, $P12_1/c1$ (No. 14), $a = 17.605(4)$ Å, $b = 8.816(1)$ Å, $c = 17.583(4)$ Å, $\beta = 117.61(1)°$, $V = 2418.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.087$, $T = 293$ K.

Source of material

The complex $[Bi(phen)_2Br_3]$ 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) and the excess of the sodium bromide. The resulting solution was stirred for 2 h at room temperature, then it was allowed to stand for 2-3 days in refrigerator. Yellow crystals of the desired product precipitated, which were filtered off, and washed with acetone and ether and air dried (0.404 g, yield 50%; mp 523 K). Elemental analyses were consistent with the stoichiometry $C_{24}H_{16}BiBr_3N_4$ (found: C, 36.1%; H, 1.74%; N, 6.8%. calc.: C, 35.6%; H, 1.97%; N, 6.9%).

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

Discussion

Bismuth complexes are of interest in the treatment of gastric ulcer [1,2]. The coordination chemistry of bismuth(III) is disproportionately sparse when compared with that of other metals [2-5]. In our research project, we want to show the nature of adducts formed between bismuth(III) bromide and aromatic *N,N'*-bidentate ligand of 1,10-phenanthroline (phen).

The crystal structure of the title compound has already been determined previously [1]. The present paper provides a more accurate refinement with lower *R*-values. Our results are basically in agreement with those of Bowmaker et al. ($R_{gt}(F) = 0.083$) [6], however, the actual refined atomic coordinates and displacement parameters are more accurate, resulting from a better crystal quality.

The complex in the solid state is a monomeric species and the environmental in bismuth atoms is seven, and the Bi atom is coordinated by four nitrogen atoms of the two 1,10-phenantroline ligands, three brom atoms of bromide anions. The arrangement of the two 1,10-phenanthroline ligands, and Br^- anions suggests coordination geometry around the bismuth(III) ions is regular and there is no gap in the enviroment of the bismuth(III) ions, possibly the lone pair of electrons on the bismuth(III) is stereoinactive. Finally, we note that throughout the above and subsequent arrays of species of diverse symmetries, 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, there is π-π stacking [1,2] interaction (charge-transfer arrays) between the parallel aromatic rings belonging to adjacent chains in two compounds.

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.05 × 0.2 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	122.67 cm^{-1}
Diffractometer, scan mode:	Siemens P3/PC, $\theta/2\theta$
$2\theta_{max}$:	54.12°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5478, 5299
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > \sigma(I_{obs})$, 3213
$N(param)_{refined}$:	289
Programs:	SHELXTL-plus [7], SHELXTL-97 [8], SADABS [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(22A)	4*e*	0.4064	0.7745	0.4320	0.055
H(1A)	4*e*	0.0997	1.0239	0.3667	0.050
H(10A)	4*e*	0.2387	0.3981	0.5518	0.059
H(21A)	4*e*	0.5478	0.7361	0.4650	0.062
H(20A)	4*e*	0.6409	0.6352	0.5957	0.059
H(14A)	4*e*	0.3477	0.5228	0.8247	0.063
H(8A)	4*e*	0.0082	0.2132	0.4433	0.065
H(13A)	4*e*	0.2624	0.6113	0.6889	0.061
H(18A)	4*e*	0.6645	0.5290	0.7394	0.076
H(3A)	4*e*	–0.1394	0.8631	0.2461	0.069
H(6A)	4*e*	–0.1158	0.3664	0.3351	0.071
H(5A)	4*e*	–0.1667	0.5937	0.2684	0.074
H(9A)	4*e*	0.1528	0.1949	0.5348	0.076
H(17A)	4*e*	0.6131	0.4850	0.8320	0.080
H(2A)	4*e*	–0.0435	1.0598	0.2732	0.065
H(15B)	4*e*	0.4895	0.4698	0.8652	0.070

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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)	4e	0.24425(2)	0.76842(3)	0.49297(2)	0.0248(1)	0.0370(2)	0.0306(2)	–0.0040(2)	0.0125(1)	–0.0012(2)
Br(2)	4e	0.17896(6)	0.8995(1)	0.59974(5)	0.0496(5)	0.0447(5)	0.0448(5)	–0.0009(4)	0.0288(4)	–0.0009(4)
Br(3)	4e	0.23037(6)	0.6575(1)	0.33839(6)	0.0389(5)	0.0699(6)	0.0418(5)	–0.0062(4)	0.0203(4)	–0.0171(4)
Br(1)	4e	0.28319(6)	1.0580(1)	0.45558(7)	0.0600(6)	0.0487(6)	0.0704(6)	–0.0148(5)	0.0395(5)	–0.0014(5)
N(1)	4e	0.0909(4)	0.8112(7)	0.3939(4)	0.030(3)	0.033(4)	0.034(3)	–0.001(3)	0.019(3)	0.000(3)
N(2)	4e	0.1517(4)	0.5414(7)	0.4789(4)	0.038(4)	0.027(4)	0.045(4)	0.005(3)	0.023(3)	0.006(3)
N(3)	4e	0.3482(4)	0.6308(8)	0.6502(4)	0.035(4)	0.051(5)	0.045(4)	0.004(3)	0.025(3)	0.011(3)
N(4)	4e	0.4127(4)	0.7019(8)	0.5392(4)	0.030(3)	0.058(5)	0.031(4)	–0.001(3)	0.014(3)	0.002(3)
C(23)	4e	0.4663(5)	0.6396(9)	0.6155(5)	0.030(4)	0.026(4)	0.035(4)	0.000(3)	0.014(3)	–0.001(3)
C(22)	4e	0.4435(5)	0.734(1)	0.4854(5)	0.028(4)	0.073(7)	0.036(4)	–0.002(5)	0.014(3)	0.006(5)
C(24)	4e	0.4326(5)	0.605(1)	0.6750(5)	0.029(4)	0.045(5)	0.037(5)	0.008(4)	0.010(4)	–0.001(4)
C(11)	4e	0.0671(5)	0.553(1)	0.4231(5)	0.045(5)	0.035(5)	0.045(5)	–0.005(4)	0.028(4)	–0.009(4)
C(1)	4e	0.0615(5)	0.944(1)	0.3556(5)	0.044(5)	0.040(5)	0.047(5)	–0.001(4)	0.027(4)	0.002(4)
C(12)	4e	0.0346(5)	0.6942(9)	0.3792(5)	0.027(4)	0.036(5)	0.038(4)	–0.003(3)	0.018(3)	–0.008(4)
C(10)	4e	0.1802(6)	0.408(1)	0.5161(6)	0.065(6)	0.034(5)	0.049(5)	0.003(5)	0.027(5)	0.005(4)
C(19)	4e	0.5538(5)	0.613(1)	0.6402(5)	0.031(4)	0.043(5)	0.046(5)	0.000(4)	0.018(4)	–0.001(4)
C(4)	4e	–0.0533(5)	0.710(1)	0.3231(5)	0.028(4)	0.057(6)	0.043(5)	–0.008(4)	0.016(4)	–0.010(4)
C(21)	4e	0.5287(6)	0.711(1)	0.5047(6)	0.048(5)	0.061(6)	0.055(6)	–0.014(5)	0.032(5)	0.001(5)
C(20)	4e	0.5837(5)	0.651(1)	0.5818(6)	0.029(4)	0.056(6)	0.059(6)	0.001(4)	0.018(4)	0.000(5)
C(7)	4e	0.0103(6)	0.431(1)	0.4082(6)	0.055(6)	0.046(6)	0.049(5)	–0.014(5)	0.035(5)	–0.017(4)
C(14)	4e	0.3707(6)	0.540(1)	0.7873(5)	0.066(6)	0.061(6)	0.038(5)	0.011(5)	0.031(5)	0.010(5)
C(16)	4e	0.4880(6)	0.544(1)	0.7565(6)	0.052(6)	0.052(6)	0.045(5)	0.018(5)	0.016(5)	0.011(5)
C(8)	4e	0.0440(7)	0.296(1)	0.4514(7)	0.067(7)	0.040(6)	0.070(7)	–0.015(5)	0.044(6)	–0.008(5)
C(13)	4e	0.3204(6)	0.597(1)	0.7058(6)	0.043(5)	0.065(6)	0.054(6)	0.000(5)	0.030(5)	0.006(5)
C(18)	4e	0.6073(6)	0.550(1)	0.7233(7)	0.040(5)	0.082(8)	0.062(7)	0.024(5)	0.019(5)	0.004(6)
C(3)	4e	–0.0816(6)	0.849(1)	0.2836(6)	0.035(5)	0.087(8)	0.048(6)	0.016(5)	0.018(4)	0.010(6)
C(6)	4e	–0.0786(6)	0.448(1)	0.3472(7)	0.049(6)	0.067(7)	0.069(7)	–0.020(5)	0.034(5)	–0.014(6)
C(5)	4e	–0.1089(6)	0.584(1)	0.3070(7)	0.027(5)	0.082(8)	0.069(7)	–0.013(5)	0.016(5)	–0.012(6)
C(9)	4e	0.1294(8)	0.285(1)	0.5055(7)	0.099(9)	0.035(5)	0.064(6)	0.001(6)	0.046(6)	0.004(5)
C(17)	4e	0.5760(6)	0.521(1)	0.7777(6)	0.046(6)	0.090(8)	0.044(6)	0.026(6)	0.004(5)	0.021(6)
C(2)	4e	–0.0244(6)	0.966(1)	0.2997(6)	0.049(6)	0.054(6)	0.054(6)	0.016(5)	0.020(5)	0.016(5)
C(15)	4e	0.4547(7)	0.511(1)	0.8116(6)	0.074(7)	0.051(6)	0.048(6)	0.018(6)	0.026(5)	0.010(5)

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