Chinese Journal of Chemistry, **2004**, *22*, 691—697 **Article**

Bismuth(III) Complexes with *N*,*N*-Di(2-hydroxylethyl)aminodithiocarboxylate: Synthesis and Crystal Structure of $\{Bi[S_2CN(C_2H_4OH)_2]_2[1,10\text{-}Phen]_2(NO_3)\}\cdot 3H_2O$ and $\{Bi[S_2CN(C_2H_4OH)_2]_3\}_2$

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Two novel one- and two-dimensional network structure bismuth(III) complexes with *N*,*N*-di(2-hydroxylethyl)-aminodithiocarboxylate, $\{Bi[S_2CN(C_2H_4OH)_2]_2[1,10\text{-}Phen]_2(NO_3)\}\cdot 3H_2O$ (**1**) and $\{Bi[S_2CN(C_2H_4OH)_2]_3\}_2$ (**2**) were synthesized. Their crystal and molecular structures were determined by X-ray single crystal diffraction analysis. The crystal **1** belongs to monoclinic system with space group *C*2/*c*, a=1.6431(7) nm, b=2.4323(10) nm, c=1.2646(5) nm, β=126.237(5)°, Z=4, V=4.076(3) nm^3, D_c=1.757 Mg/m^3, μ=4.598 mm^{-1}, F(000)=2156, R=0.0211, wR=0.0369. The structure shows a distorted square antiprism configuration with eight-coordination for the central Bi atom. The one-dimensional chain structure was formed by H-bonding interaction between hydroxyl group of *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate ligands and crystal water. The crystal **2** belongs to monoclinic system with space group *P*2(1)/*c*, a=1.1149(4) nm, b=2.1274(8) nm, c=2.2107(8) nm, β=98.325(8)°, Z=4, V=5.188(3) nm^3, D_c=1.920 Mg/m^3, μ=7.315 mm^{-1}, F(000)=2944, R=0.0565, wR=0.0772. The structure shows a distorted square antiprism configuration with eight-coordination for the central Bi atoms. The two-dimensional network structure was formed by H-bonding interaction between adjacent molecules.

Keywords bismuth(III) complex, *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate, one- and two-dimensional network, crystal structure

Introduction

The chemistry of organotin(IV) dithiocarbamate complexes was extensively studied due to their biological activities.[1-5] To date, a large number of transition-metal complexes with dithiocarbamate have been synthesized and structurally characterized,[6-9] including $Ni(S_2CNC_4H_8O)_2$, $Cu(S_2CNC_4H_8)_2$, $Zn(S_2CNC_4H_8O)_2$ and $Fe(S_2CNC_4H_8O)_2$(DMF). However, the chemistry of main-group metal complexes with dithiocarbamate has been scarcely studied, and few reports have appeared on the syntheses and structures of the bismuth(III) complexes with dithiocarbamate.[10] As a continuation of our interest in sulfur-containing ligands, we report here the synthesis and structure of two novel bismuth(III) complexes with *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate, $\{Bi[S_2CN(C_2H_4OH)_2]_2[1,10\text{-}Phen]_2(NO_3)\}\cdot 3H_2O$ (**1**) and $\{Bi[S_2CN(C_2H_4OH)_2]_3\}_2$ (**2**).

Experimental

Gerenal procedure

Sodium *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate were prepared by the method described in literature.[11] The elemental analyses were performed on a PE-2400-II elemental analyzer. IR spectra were recorded on a Nicolet-460 spectrophotometer, as KBr discs. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo Kα (λ=0.071073 nm) radiation.

Synthesis of complexes 1 and 2

Complex 1 To an aqueous solution of $Bi(NO_3)_3\cdot 5H_2O$ (1.0 mmol) and mannite (1.0 mmol) was added an aqueous solution of sodium *N*,*N*-di(2-hydroxylethyl)-aminodithiocarboxylate (2.0 mmol) and phenanthroline (2.0 mmol) and the resultant solution stirred for 1.0 h at 30 ℃. The yellow solid was obtained by filtration. The product was recrystallized from acetonitrile to give yellow crystals 0.82 g, yield 86%, m.p. 145 ℃ (dec); IR (KBr) ν: 3353, 2975, 2864, 1473, 1089, 958, 455 cm^{-1}; Anal. calcd for $C_{34}H_{42}BiN_7O_{10}S_4$ (M_r = 1045.97): C 39.04, H 4.05, N 9.37, S 12.26; found C 39.31, H 4.12, N 9.18, S 12.07.

Complex 2 To an aqueous solution of $Bi(NO_3)_3\cdot 5H_2O$ (1.0 mmol) and mannite (1.0 mmol) was added an aqueous solution of sodium *N*,*N*-di(2-hydroxylethyl)-

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aminodithiocarboxylate (3.0 mmol) and stirred for 0.5 h at 30 ℃. The yellow solid was obtained by filtration. The product was recrystallized from acetonitrile to give yellow crystals 0.60 g, yield 80%, m.p. 115 ℃ (dec); IR (KBr) *v*: 3345, 2961, 2854, 1482, 1064, 942, 449 cm^{-1}. Anal. calcd for $C_{30}H_{60}Bi_2N_6O_{12}S_{12}$ (M_r=1499.52): C 24.03, H 4.03, N 5.60, S 25.66; found C 24.34, H 3.95, N 5.79, S 25.54.

Crystallographic measurement

The yellow crystal with dimensions 0.15 mm×0.10 mm×0.05 mm (**1**) or 0.20 mm×0.15 mm×0.10 mm (**2**) was mounted in a fiber, respectively. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo Kα (λ=0.071073 nm) radiation. The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on F^2 (Table 1). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically.

Results and discussion

IR spectra of complexes 1 and 2

The assignment of IR bands of two complexes has been made by comparison with the IR spectra of related complexes with sodium *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate. A new absorption band appears at 455 and 449 cm^{-1} which are characteristic vibrations of Bi—S bond formed.

One obvious feature of the IR spectra is the similarity of the stretching bands arising from the *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate groups. The relatively high value (1473 and 1482 cm^{-1}) for ν(C—N) is similar to that reported for analogous tin complexes.[12-15] It is suggested that the *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate groups of the two complexes are linked to Bi atom in a bidentate fashion.

In IR spectra, the important bands arising from $\nu(CS_2)_{asym}$ and $\nu(CS_2)_{sym}$ appear at 1089, 958 cm^{-1} and 1064, 942 cm^{-1}, respectively. The $\Delta\nu$ values [$\nu(CS_2)_{asym} - \nu(CS_2)_{sym}$] are 131 and 122 cm^{-1}, which are much smaller than the $\Delta\nu^*$ for the R_2NCS_2R',[16] but are larger than the $\Delta\nu'$ for the corresponding sodium dithiocarbamate.[11] This shows that the *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate groups are coordinated to Bi atom in an anisobidentate fashion.[17]

Crystal and molecular structures of complexe 1

The molecular structure is shown in Figure 1. Table 2 gives the atomic coordinates and equivalent isotropic thermal parameters. The selected bond lengths and angles are listed in Table 3.

Complex **1** consists of $Bi[S_2CN(C_2H_4OH)_2]_2$ [1,10-Phen]$^+$ cation and the nitrate anion. The nitrate anion in general position balances the charge. The crystal structure of complex **1**, as shown in Figure 1, consists of one complex molecule and three solvating water molecules. Four nitrogen atoms from the two chelating phenanthroline ligands and four sulfur atoms from the

Table 1 Crystallographic data of complexes **1** and **2**

	1	**2**
Molecular formula	$C_{34}H_{42}BiN_7O_{10}S_4$	$C_{30}H_{60}Bi_2N_6O_{12}S_{12}$
Formular weight	1045.97	1499.52
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
Unit cell dimensions		
a/nm	1.6431(7)	1.1149(4)
b/nm	2.4323(10)	2.1274(8)
c/nm	1.2646(5)	2.2107(8)
β/(°)	126.237(5)	98.325(8)
Volume/nm^3	4.076(3)	5.188(3)
Z	4	4
D_c/(Mg•m^{-3})	1.705	1.920
F(000)	2156	2944
Scan range θ/(°)	2.95≤θ≤25.03	1.34≤θ≤25.03
Total/unique/R_{int}	10658/3596/0.0272	23351/7422/0.2715
μ/mm^{-1}	4.589	7.315
R_1/wR_2	0.0211/0.0369	0.0565/0.0772
ρ_{max}/ρ_{min}/(e•nm^{-3})	$4.19\times10^2/-3.98\times10^2$	$8.72\times10^2/-1.121\times10^3$

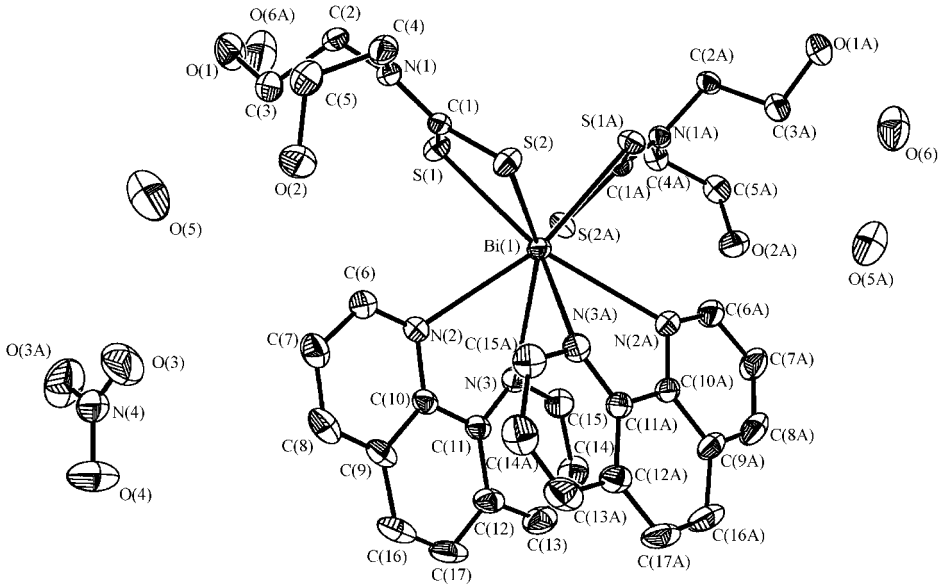

Figure 1 Molecular structure of complex **1**.

Table 2 Atomic coordinates ($\times 10^4$) and thermal parameters ($nm^2 \times 10^5$) for complex **1**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
Bi(1)	5000	3404(1)	7500	34(1)	C(3)	1976(2)	4614(1)	7568(3)	50(1)
N(1)	3845(2)	4534(1)	9186(2)	34(1)	C(4)	4223(2)	4524(1)	10570(3)	46(1)
N(2)	3424(2)	2798(10)	7144(3)	43(1)	C(5)	3474(3)	4271(1)	10756(3)	52(1)
N(3)	4173(2)	2504(1)	5777(2)	43(1)	C(6)	3029(2)	2932(1)	7768(3)	52(1)
N(4)	0	2193(2)	7500	63(1)	C(7)	2609(3)	2555(2)	8139(4)	62(1)
O(1)	1235(2)	4992(1)	6705(2)	71(1)	C(8)	2602(3)	2019(2)	7866(4)	64(1)
O(2)	3178(2)	3737(1)	10221(2)	63(1)	C(9)	3004(2)	1850(1)	7202(3)	48(1)
O(3)	696(2)	2428(1)	8478(4)	114(1)	C(10)	3404(2)	2260(1)	6842(3)	39(1)
O(4)	0	1690(2)	7500	94(1)	C(11)	3812(2)	2102(1)	6144(3)	40(1)
O(5)	1096(3)	3621(2)	8780(4)	121(1)	C(12)	3833(2)	1543(1)	5879(3)	50(1)
O(6)	9276(3)	4684(2)	5724(4)	110(1)	C(13)	4251(3)	1409(2)	5221(4)	67(1)
S(1)	3722(1)	4230(1)	7085(1)	41(1)	C(14)	4581(3)	1809(2)	4819(4)	66(1)
S(2)	5297(1)	3827(1)	9766(1)	43(1)	C(15)	4526(2)	2356(1)	5117(3)	53(1)
C(1)	4253(2)	4225(1)	8738(3)	33(1)	C(16)	3059(3)	1290(1)	6926(4)	67(1)
C(2)	2988(2)	4900(1)	8325(3)	39(1)	C(17)	3456(3)	1140(1)	6313(4)	66(1)

Table 3 Selected bond distances (nm) and angles (°) of complex **1** [a]

Bi(1)—S(1)#1	0.27217(11)	Bi(1)—S(2)	0.28016(14)
Bi(1)—S(1)	0.27217(11)	Bi(1)—S(2)#1	0.28016(14)
Bi(1)—N(2)#1	0.2777(2)	Bi(1)—N(3)	0.2810(3)
Bi(1)—N(2)	0.2777(2)	N(1)—C(1)	0.1337(3)
Bi(1)—N(3)#1	0.2810(3)	N(1)—C(2)	0.1465(3)
S(1)—C(1)	0.1725(3)	S(2)—C(1)	0.1712(3)
S(1)#1-Bi(1)-S(1)	84.98(5)	S(1)#1-Bi(1)-N(2)#1	79.72(6)
S(1)-Bi(1)-N(2)#1	164.24(5)	S(1)#1-Bi(1)-N(2)	164.24(5)
S(1)-Bi(1)-N(2)	79.72(6)	N(2)#1-Bi(1)-N(2)	115.77(10)

Continued

S(1)#1-Bi(1)-S(2)	83.36(3)	S(1)-Bi(1)-S(2)	64.86(3)
N(2)#1-Bi(1)-S(2)	116.56(6)	N(2)-Bi(1)-S(2)	86.71(6)
S(1)#1-Bi(1)-S(2)#1	64.86(3)	S(1)-Bi(1)-S(2)#1	83.36(3)
N(2)#1-Bi(1)-S(2)#1	86.71(6)	N(2)-Bi(1)-S(2)#1	116.56(6)
S(2)-Bi(1)-S(2)#1	137.00(4)	S(1)-Bi(1)-N(3)	117.45(6)
N(2)#1-Bi(1)-N(3)	71.85(7)	N(2)-Bi(1)-N(3)	58.83(8)
S(2)-Bi(1)-N(3)	142.27(6)	S(2)#1-Bi(1)-N(3)	77.33(6)
O(3)#2-N(4)-O(4)	117.9(3)	O(3)-N(4)-O(3)#2	124.2(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+3/2$; #2 $-x, y, -z+3/2$.

N,*N*-di(2-hydroxylethyl)aminodithiocarboxylate groups ligate to the Bi(III) ion, forming a distorted square antiprism geometry. One NO_3 anion and three water molecules exist outside the cation $Bi[S_2CN(C_2H_4OH)_2]_2[1,10\text{-Phen}]^+$ as a counter ion and solvating molecule, respectively.

In this complex, there are two shorter Bi—S bonds [Bi(1)—S(1), Bi(1)—S(1)#1 0.27217(11) nm] and two longer Bi—S bonds [Bi(1)—S(2), Bi(1)—S(2)#1 0.28016(14) nm]. All the two shorter bonds indicate a strong S coordination, while the other set corresponds to a weaker interaction. It is noticeable that in the two *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate groups the C—S bond associated with the strong Bi—S is slightly longer [S(1)—C(1), 0.1725(3) nm] than that [S(2) —C(1) 0.1712(3) nm] associated with the weaker Bi—S bond, showing clearly the double bond character.[18] In addition, the two chelating phenanthroline ligands are bonded to the bismuth through the four nitrogen atoms. The Bi—N distances for Bi(1)—N(2) and Bi(1)—N(2)#1 are 0.2777(2) nm, and for Bi(1)—N(3) and Bi(1)—N(3)#1 are 0.2810(3) nm, falling in the same range in other analogous Bi/N complex.[19] Both the phenanthroline molecules are nearly planar, and the largest deviation from their respective mean plane is 0.00211 nm. The mean plane of the two phenanthroline molecules are inclined at 82.5°.

In this complex, because the *N*,*N*-di(2-hydroxylethyl)-aminodithiocarboxylate groups and phenanthroline ligands bond with Bi atom in bidentate fashion by the four nitrogen atoms of the phenanthroline ligands and the four sulfur atoms of the *N*,*N*-di(2-hydroxylethyl)-aminodithiocarboxylate groups, the angles of N-Bi-N and S-Bi-S deviate from the standard square antiprism angle. For example: the angles of the four nitrogen atoms and the four sulfur atoms around Bi(1) atom are N(2)-Bi(1)-N(3) = N(2)#1-Bi(1)-N(3)#1 = 58.83(8)°, S(1)-Bi(1)-S(2) = S(1)#1-Bi(1)-S(2)#1 = 64.86(3)°. From this, the Bi atom of this complex is of distorted square antiprism geometry.

The hydrogen bonding plays an important role in consolidating the crystal structure. In each molecule of complex **1**, the NO_3 anion links the hydroxyl group of the *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate ligands of the cation through O···H—O hydrogen bonding with the O(3)···O(5) distance of 0.2950 nm. Intermolecular hydrogen bonding interaction is observed between the NO_3 and the hydroxyl group of *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate of neighboring molecule (0.3011 nm). In addition, the hydrogen bonds are also found between the solvating H_2O and the *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate ligand with the O···O distances of 0.2777—0.2784 nm. It can be seen that each $Bi[S_2CN(C_2H_4OH)_2]_2[1,10\text{-Phen}]^+$ cation is further connected to other $Bi[S_2CN(C_2H_4OH)_2]_2[1,10\text{-Phen}]^+$ cations through NO_3 anions, and the water molecules serve as oxygen bridges to form the one-dimensional chain structure.

Crystal and molecular structures of complexe 2

The molecular structure is shown in Figure 2. Table 4 gives the atomic coordinates and equivalent isotropic thermal parameters. The selected bond lengths and angles are listed in Table 5. Two independent molecules of complex **2** are present in the structure so that the asymmetric unit is formed by one half of both molecules and a total of four molecules comprise the unit cell. In any case, although independent from a crystallographical point of view, all molecules have the same structure with comparable values for bond lengths and angles. Two of the six bidentate ligands are bridged in such a way that each sulfur atom is simultaneously bonded to both Bi atoms. As a result, the Bi atoms are eight-coordinated in a coordination polyhedron that can be described as distorted square antiprism. A view of complex **2** is shown in Figure 2 from which it is evident that a longer Bi—S intermolecular interaction is present resulting in a centrosymmetric dimeric structure. Two sets of Bi—S distances are observed: mean Bi—S= 0.2730(7) nm [Bi(1)—S(4) 0.2627(7) nm, Bi(1)—S(3) 0.2761(7) nm, Bi(1)—S(1) 0.2703(6) nm, Bi(1)—S(2) 0.2828(7) nm] and 0.3110(7) nm [Bi(1)—S(5) 0.3087(7) nm, Bi(1)—S(5)#1 0.3115(7) nm, Bi(1)—S(6) 0.3142(7) nm, Bi(1)—S(6)#1 0.3096(7) nm], and similarly two sets of S-Bi-S angles: 68.6(5)° and 56.8(3)° [S(1)-Bi(1)-S(2) 65.6(8)°, S(4)-Bi(1)-S(3) 65.6(3)°, S(5)-Bi(1)-S(6) 56.7(4)°, S(6)#1-Bi(1)-S(5)#1 56.9(2)°]. Inspection of bond lengths clearly shows that the

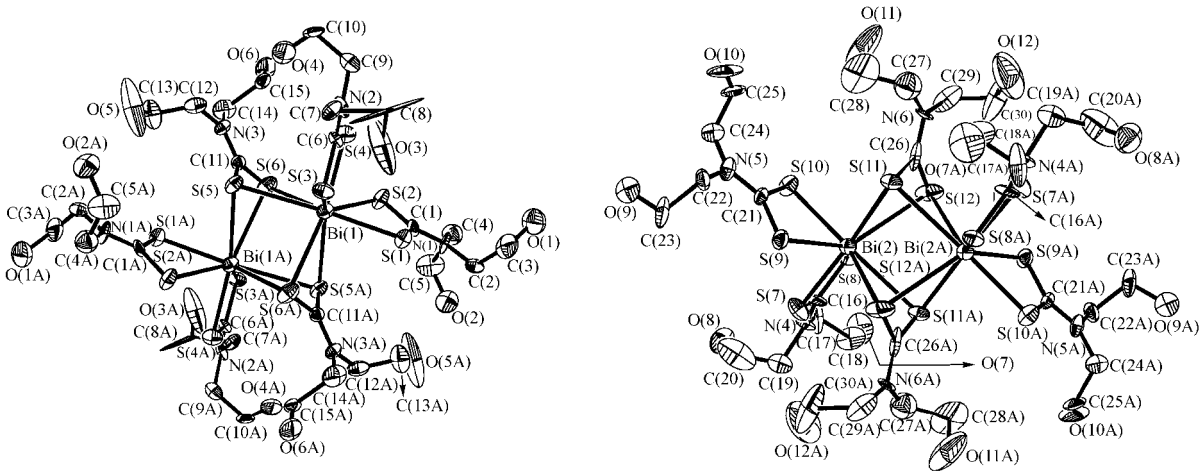

Figure 3 Molecular structure of complex **2**.

Table 4 Atomic coordinates ($\times 10^4$) and thermal parameters ($nm^2 \times 10^5$) for complex **2**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
Bi(1)	3926(1)	5604(1)	9597(1)	47(1)	S(12)	−11155(6)	5595(4)	5652(3)	85(3)
Bi(2)	−8933(1)	4659(1)	5688(1)	46(1)	C(1)	1360(20)	5287(13)	8840(11)	58(8)
N(1)	460(20)	5048(10)	84929(9)	54(7)	C(2)	290(20)	5046(12)	7854(12)	48(8)
N(2)	4362(15)	7690(11)	9471(9)	42(6)	C(3)	−120(20)	5618(18)	7509(14)	111(17)
N(3)	5254(19)	6052(9)	11602(9)	42(6)	C(4)	−530(20)	4786(17)	8774(12)	88(14)
N(4)	−9570(20)	2778(11)	6570(11)	66(7)	C(5)	−250(30)	4055(17)	8951(16)	97913)
N(5)	−5289(19)	5399(10)	6604(10)	54(6)	C(6)	4257(18)	7068(11)	9513(9)	28(6)
N(6)	−10260(20)	6774(10)	5816(10)	49(7)	C(7)	5330(20)	8002(11)	9173(10)	53(9)
O(1)	−1343(19)	5784(10)	7578(9)	119(8)	C(8)	4730(30)	8396(19)	8407(18)	160(12)
O(2)	−282(19)	3697(9)	8416(10)	101(8)	C(9)	3710(20)	8124(12)	9807(12)	56(9)
O(3)	4880(20)	7920(14)	8281(16)	220(19)	C(10)	4290(20)	8377(14)	10395(14)	67(10)
O(4)	4617(19)	7832(13)	10793(10)	139(11)	C(11)	5196(19)	5704(11)	11108(11)	40(7)
O(5)	8240(30)	6700(20)	11999(16)	280(20)	C(12)	6190(30)	6514(13)	11783(11)	60(10)
O(6)	2507(17)	6209(10)	12360(8)	96(7)	C(13)	7370(30)	6358(17)	12089(15)	94(14)
O(7)	−12380(20)	2351(11)	7038(12)	153(11)	C(14)	4500(30)	5938(13)	12081(13)	92(17)
O(8)	−7740(20)	2013(10)	7380(11)	121(8)	C(15)	3360(20)	6410(15)	11888(13)	76(10)
O(9)	−2810(16)	4830(8)	7001(9)	82(6)	C(16)	−9370(20)	3343(12)	6361(12)	54(8)
O(10)	−4680(20)	6739(9)	6941(9)	133(10)	C(17)	−10470(30)	2637(19)	7012(16)	123(16)
O(11)	−8660(20)	7365(18)	6718(13)	260(20)	C(18)	−11550(30)	2434(17)	6634(18)	140(20)
O(12)	−12060(20)	7650(20)	5358(14)	300(30)	C(19)	−8840(30)	2199(16)	6382(17)	91(13)
S(1)	2543(6)	5607(3)	8486(3)	53(2)	C(20)	−7670(30)	2153(19)	6770(20)	170(30)
S(2)	1461(6)	5307(4)	9619(3)	67(2)	C(21)	−6280(20)	5134(11)	6310(11)	50(8)
S(3)	5135(6)	6581(3)	9125(3)	57(2)	C(22)	−4230(20)	5392(12)	6261(11)	63(11)
S(4)	3180(6)	6728(3)	9866(3)	59(2)	C(23)	−3390(20)	4822(14)	6366(14)	94(15)
S(5)	6134(6)	5848(3)	10583(3)	53(2)	C(24)	−5130(20)	5681(13)	7199(11)	66(12)
S(6)	4085(6)	5128(4)	10951(3)	69(2)	C(25)	−5440(30)	6332(15)	7228(13)	87(13)
S(7)	−8248(7)	3465(3)	5920(3)	69(2)	C(26)	−10093(19)	6213(15)	5573(12)	63(9)
S(8)	−10220(6)	3986(3)	6520(3)	59(2)	C(27)	−9260(30)	7216(12)	5748(19)	120(20)
S(9)	−6475(5)	4823(3)	5600(3)	55(2)	C(28)	−8140(40)	7170(20)	6192(16)	200(30)
S(10)	−7566(6)	5116(3)	6707(3)	61(2)	C(29)	−11320(30)	6920(16)	6102913)	105(15)
S(11)	−8966(6)	5990(3)	5167(3)	53(2)	C(30)	−12500(30)	7160(30)	5706(18)	210(40)

Table 5 Selected bond distances (nm) and angles (°) of complex **2** [a]

Bi(1)—S(4)	0.2627(7)	Bi(1)—S(1)	0.2703(6)
Bi(1)—S(3)	0.2761(7)	Bi(1)—S(2)	0.2828(7)
Bi(1)—S(5)	0.3087(7)	Bi(1)—S(6)#1	0.3096(7)
Bi(1)—S(5)#1	0.3115(7)	Bi(1)—S(6)	0.3142(7)
Bi(2)—S(7)	0.2681(7)	Bi(2)—S(10)	0.2711(7)
Bi(2)—S(9)	0.2797(6)	Bi(2)—S(8)	0.2873(7)
Bi(2)—S(11)	0.3054(6)	Bi(2)—S(11)#2	0.3113(7)
Bi(2)—S(12)#2	0.3027(7)	Bi(2)—S(12)	0.3169(7)
S(1)—C(1)	0.177(2)	S(2)—C(1)	0.171(2)
S(3)—C(6)	0.173(2)	S(4)—C(6)	0.169(2)
S(5)—C(11)	0.170(2)	S(6)—C(11)	0.174(2)
S(7)—C(16)	0.172(2)	S(8)—C(16)	0.173(2)
S(9)—C(21)	0.169(2)	S(10)—C(21)	0.178(2)
S(11)—C(26)	0.171(3)	S(12)—C(26)	0.180(2)
S(4)-Bi(1)-S(1)	89.6(2)	S(4)-Bi(1)-S(3)	65.6(3)
S(1)-Bi(1)-S(3)	84.4(2)	S(4)-Bi(1)-S(2)	81.9(2)
S(1)-Bi(1)-S(2)	65.6(8)	S(3)-Bi(1)-S(2)	134.7(2)
S(4)-Bi(1)-S(5)	86.2(2)	S(1)-Bi(1)-S(5)	158.9(1)
S(3)-Bi(1)-S(5)	75.9(5)	S(2)-Bi(1)-S(5)	134.6(4)
S(4)-Bi(1)-S(6)#1	144.6(2)	S(1)-Bi(1)-S(6)#1	89.5(9)
S(3)-Bi(1)-S(6)#1	79.3(5)	S(2)-Bi(1)-S(6)#1	130.3(2)
S(5)-Bi(1)-S(6)#1	79.5(2)	S(4)-Bi(1)-S(5)#1	158.4(2)
S(1)-Bi(1)-S(5)#1	83.5(3)	S(3)-Bi(1)-S(5)#1	134.5(1)
S(2)-Bi(1)-S(5)#1	77.1(2)	S(5)-Bi(1)-S(5)#1	104.9(1)
S(4)-Bi(1)-S(6)	93.0(4)	S(1)-Bi(1)-S(6)	144.3(1)
S(3)-Bi(1)-S(6)	129.6(9)	S(2)-Bi(1)-S(6)	80.3(2)
S(5)-Bi(1)-S(6)	56.7(4)	S(6)#1-Bi(1)-S(5)#1	56.9(2)
S(7)-Bi(2)-S(10)	94.0(2)	S(7)-Bi(2)-S(9)	82.9(2)
S(10)-Bi(2)-S(9)	64.8(1)	S(7)-Bi(2)-S(8)	63.8(8)
S(7)-Bi(2)-S(10)	89.1(3)	S(9)-Bi(2)-S(8)	133.7(2)
S(7)-Bi(2)-S(12)#2	88.3(2)	S(10)-Bi(2)-S(12)#2	141.5(8)
S(9)-Bi(2)-S(12)#2	77.5(1)	S(8)-Bi(2)-S(12)#2	128.9(2)
S(7)-Bi(2)-S(11)	159.7(3)	S(10)-Bi(2)-S(11)	87.5(2)
S(9)-Bi(2)-S(11)	79.4(5)	S(8)-Bi(2)-S(11)	136.3(3)
S(12)#2-Bi(2)-S(11)	78.3(2)	S(7)-Bi(2)-S(11)#2	82.2(2)
S(10)-Bi(2)-S(11)#2	161.2(7)	S(9)-Bi(2)-S(11)#2	132.2(1)
S(8)-Bi(2)-S(11)#2	76.4(6)	S(12)#2-Bi(2)-S(11)#2	56.9(3)
S(11)-Bi(2)-S(11)#2	102.4(5)	C(1)-S(1)-Bi(1)	87.9(8)
C(1)-S(2)-Bi(1)	85.0(9)	C(6)-S(3)-Bi(1)	85.5(8)
C(6)-S(4)-Bi(1)	90.9(8)	C(11)-S(5)-Bi(1)	86.9(8)
C(11)-S(5)-Bi(1)#1	84.5(9)	C(11)-S(6)-Bi(1)#1	84.4(8)
Bi(1)-S(5)-Bi(1)#1	75.1(1)	C(16)-S(7)-Bi(2)	92.3(9)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+2$; #2 $-x-2$, $-y+1$, $-z+1$.

non-bridging S atoms form coordination bonds that are shorter than those of the bridging S atoms. In addition, one of the two Bi—S bonds of each non-bridging and bridging ligand is always significantly shorter than the other.

In crystal of complex **2**, the hydroxyl group oxygen atoms of the *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate ligands are hydrogen bonded to the hydroxyl groups of the *N*,*N*-di(2-hydroxylethyl)aminodithiocarboxylate of the neighboring molecules through O—H···O (O···O, 0.2618—0.2827 nm), forming a two-dimensional network structure.

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